



Control of electrodeposit properties of nickel and nickel alloy by pulse plating.

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CONTROL OF ELECTRODEPOSIT PROPERTIES OF NICKEL
AND NICKEL ALLOY BY PULSE PLATING

BY

SEYED ESMAIL HADIAN

A THESIS SUBMITTED TO THE COUNCIL
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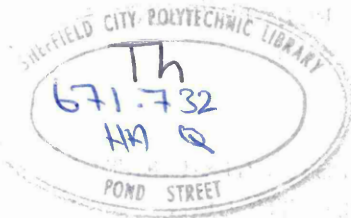
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PREFACE

The work described in this thesis was carried out at Sheffield City Polytechnic between the 1st March 1986 and May of 1989, under the Dr R.P. Stratton Director of Studies, and Dr E. Jackson acted as adviser to August 1988. According to the regulations, a course in Metallurgical Process Management must be successfully completed. The details of the course are given below;

MODULE 1

- (a) PROCESS METALLURGY
- (b) MECHANICAL METALLURGY
- (c) ADVANCED THERMODYNAMICS

MODULE 2

- (a) ACCOUNTANCY
- (b) MICRO-ECONOMICS AND FINANCIAL CONTROL
- (c) COMPUTATIONAL METHODS AND OPERATIONAL RESEARCH

MODULE 3

- (a) CORROSION RESISTANT AND HIGH TEMPERATURE METALS AND ALLOYS
- (b) POWDER METALLURGY
- (c) CONTINUOUS CASTING

MODULE 4

CASE STUDIES

The candidate's performance during the above mentioned courses was assessed by means of written examinations and continuous assessment of specific assignments.

DECLARATION

During the period of registration for the CNAA degree of MPhil the candidate has not been registered for any other CNAA award or for a university degree.

The results and theories presented in thesis are original except where reference is made to previous work.

Signed :

Date : Nov 1990

S.E.HADIAN

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CONTROL OF ELECTRODEPOSIT PROPERTIES OF NICKEL AND NICKEL
ALLOY BY PULSE PLATING

ABSTRACT

Pulsed-current electrolysis with various ratios of 'on'-time to 'off'-time have been applied to the deposition of Ni and Ni/Fe alloys from Watts and Ni/Fe baths.

The electro-depositions of nickel and nickel-iron alloy on copper and mild-steel substrates using Watts and Ni/Fe baths have been investigated. The mechanical properties of micro-hardness and internal stress obtained using the EFCO stress-meter and X-ray diffraction were measured as a function of bath composition, 'on'/'off' cycles, current density, types of plating and solution pH.

The structure and composition of alloys deposited have been investigated using S.E.M and wet analyses. It has been shown that the composition of the Ni/Fe alloy deposits changed markedly with increasing current density and proved to be dependent on current density. Also, the composition and properties of electrodeposited Ni/Fe alloy have been related to the composition of electrolyte and the deposition conditions.

Distinct differences between direct and pulsed processes revealed themselves in the surface characteristics, micro-hardness data, cathode current efficiency data, internal stress measurements, pH data, various current density and finally composition of platings. Implications of using pulse plating to control the quality of electrodeposits have been considered.

CONTENT

	<u>PAGE</u>
1.0-INTRODUCTION	9
2.0-LITERATURE SURVEY	11
2.1-Basic electroplating theory	11
2.2-The terminology of pulse plating	12
2.3-Origins and developments of electroplating	14
2.3.1-Historical origins	14
2.3.2-Applications of electroplating	15
2.3.3-Electroforming	16
2.3.4-Nickel-Iron alloys	18
2.3.5-Pulse plating of Ni alloys	21
2.4-Mechanism of general electrodeposition	23
2.4.1-Mechanism of alloy deposition	26
2.5-Electrode potentials	30
2.6-Electrolytic crystallization	33
2.7-Nickel plating solutions	36
2.7.1-Watts nickel plating solution	36
2.7.2-Bath composition and operating conditions	38
2.7.3 The nickel-iron plating	39
2.8-The origins of residual stress in electrodeposits	
2.8.1-The crystallite-joining theories	41
2.8.2-Hydrogen theories	44
2.8.3-Changes in foreign substances theories	46
2.8.4-Excess-energy theories	46
2.8.5-Lattice-defects theories	48
2.9-The measurement of macrostress	50
2.9.1-Principles and problems of stress measurement	51

2.9.2-Problems arising from use of stop-off materials	54
2.9.3-Effect of temperature change	54
2.9.4-Calibration of stressmeters	56
3.0-EXPERIMENTAL METHOD	
3.1-General description of the equipments	58
3.1.1-Power Mosfets	58
3.1.2-Oscilloscope	59
3.1.3-Power supply	59
3.1.4-Pulse generator	60
3.1.5-Copper coulometer	60
3.1.6-The EFCO-meter/Dilatometer,	61
3.1.6.1- Principle of operating of EFCO meter	61
4.0-EXPERIMENTAL DETAILS	
4.1-Preparation of substrates	62
4.2-Preparation of Watts plating solution	62
4.3-Nickel-iron solutions	63
4.4-Preparation of copper substrate as cathodes for plating	65
4.5-Progressive electrolytic purification of plating solution via 'dummying'	66
4.5.1-Dummying	66
4.6-Use of conventional plating for varying current densities of Ni/Fe solutions	67
4.7-Operation of periodic pulse plating	68
4.8-Plating and use of stressmeter using the strip mild steel specimens	69
4.9-Micro-hardness determination	70
4.9.1-Scanning electron microscopy(S.E.M)	71
4.9.2-Wet analysis	71

4.9.3-Adhesion determination	71
4.9.4- Current efficiency determination	72
4.9.5-Using x-ray diffraction to determine the stress within deposits	72
5.0-EXPERIMENTAL RESULTS	
5.1-Effect of current density on pulse and conventional plating	74
5.1.1-Pulse plating	74
5.1.2-Conventional plating	77
5.2-Effect of concentration of electrolyte on types of plating	78
5.3-Effect of pH on types of plating	80
5.4-Influence of duration of electrolysis on types of plating	81
5.5-Effect of coating thickness with types of plating and different substrates used	82
6.0-DISCUSSION	
6.1-Effects of current densities upon deposits	83
6.2-Effects of plating conditions upon composition of Ni/Fe alloys	85
6.3-Effect of coating thickness with types of plating	91
6.4-Effect of on-time to off-time	92
7.0-CONCLUSIONS	95
8.0-SUGGESTIONS FOR FUTURE WORK	97
9.0-REFERENCES	99

1.0-INTRODUCTION

Pulse plating has gained acceptance in some sectors of the metal finishing industry, especially electronics, gold plating and finally decorative applications. The pulsed current has beneficial effects on deposit properties, for example, many investigators⁽¹⁻²⁾ have reported that coatings with fine grain structure, high purity and low electrical resistance can be obtained for copper, silver, gold and palladium.

Pulse plating can be defined as a method of electroplating by means of an 'on-off' direct current or potential in place of the continuous direct current used in conventional plating. Electrodeposition of metals using pulsed-current electrolysis has been extensively studied in recent years⁽¹⁻⁴⁾. Metals deposits produced by pulsed-current electrolysis have many properties distinguishing them from those obtained by direct current electrolysis. Nickel and nickel-iron alloy deposits have a number of applications as decorative⁽⁵⁾, electroformed⁽⁶⁾ and finally magnetic⁽⁷⁾ materials.

A study of the effect of the plating variables on the electrodeposition of the nickel and nickel-iron alloy deposits has been reported by others⁽⁸⁻⁹⁾. Advantages of pulse plating were most frequently cited in this field. A higher average cathodic current density can be applied to the plating system for deposition due to the higher average concentration of metal ion in the diffusion layer.

The aim of the research is:

to investigate the relationship between the processing conditions in a pulse plating bath and the properties of electrodeposited metal coatings. Also parameters controlling the formation of low stressed deposits and coherent alloy coatings of predetermined composition is to be established.

A plating unit is to be designed and constructed and electrodeposits formed using a D.C power supply having a variable 'on' pulse time and variable 'off' relaxation time.

The initial work will be concerned with evaluating the stresses within the deposits from Watts and Ni/Fe solutions, and these stresses were measured using both mechanical (dilatometric method) and X-ray techniques.

The deposits from the Watts and Ni/Fe baths and their mechanical properties (hardness and internal stress) are discussed in detail as a function of bath composition ,current density ,pH solution,thickness, plating time and 'off'-time .

2.0 LITERATURE SURVEY

2.1 BASIC ELECTROPLATING THEORY⁽¹⁰⁻¹²⁾

Electrodeposition is the process of depositing a metallic coating or other conductive layer on surfaces by means of electrolysis or electrochemical processes i.e. passage of current from an anode of the metal which is to be deposited, to the cathode on which the deposit is to be obtained by using Faraday's law.

The amount of metal theoretically deposited may be calculated as follows;

$$W = ItA/ZF \dots \dots \dots (1)$$

where; W = weight of metal deposited

A = atomic weight of metal deposited

Z = valency of deposited metal

F = Faraday's constant

t = Plating time, Second

I = Current in *Amps*

from (1) it follows that;

$$\begin{array}{l} \text{Atomic weight of component} \\ \text{1 gramme chemical equivalent} = \frac{\text{-----}}{\text{Valency of above component}} \end{array}$$

Faraday's law states two principles;

(a) For the current (It), the weight of metal deposited is directly proportional to its chemical equivalent.

(b) The weight (W) of metal deposited is directly proportional to the quantity of electricity passed i.e. current (I)*Time(sec).

One Faraday (96,490 Amp.secs) of electricity yields 1

^{equivalent}
gramme. λ THE CHEMICAL EQUIVALENT can be defined as the weight of the component which will replace or combine eight parts of oxygen by weight.

THE VALENCY can be defined as the number of atoms of hydrogen which replace or combine with one atom of element or substance.

Therefore, for chromium deposition from the hexavalent state, 96,500 coulombs (ampere seconds) deposit 8.67 grams of chromium.

1 coulomb therefore deposits $8.67/96,500$ grams of chromium.

One ampere hour is 1 ampere flowing for 3,600 seconds ie, 3,600 as coulomb.

Therefore 1 ampere hour deposits $(8.67 \times 3,600)/96,500 = 0.323$ grams of chromium.

2.2 THE TERMINOLOGY OF PULSE PLATING

Pulse plating can be defined as current-interrupted electroplating. Figure 1 shows the typical square-wave form. Figure 2 is a typical oscilloscope trace of a square wave attainable with existing pulse equipment. However, the figure does not show a pure square wave because there is a gradual curvature to both the ascending and descending current flows. The curvature on the rising flow is intentionally induced electronically to avoid an instantaneous rise and current overshoot.

This type of pulse process is suggested as a means of obtaining smooth and bright deposits. If, for example, dc flows for five sec and is interrupted for one sec between

periods of flow, there is greater opportunity for replenishment of the cathode film through diffusion and convection. Cathode polarization is decreased, and cathode efficiency may be increased. Consequently, a higher current density can be used and a desired thickness can be deposited in less time, even though the current is not flowing continuously. In pulse electrolysis, selection of the electrolyte, peak current density, on-time, and off-time determine the physical characteristics of the electrodeposits.

The process of pulse plating is that during the period when the current is on, the metal ions next to the cathode are depleted as in the normal way, but during the time that the current is off, the processes of mass transport via diffusion, ionic migration and convection, (both natural, and forced by agitation), have time to replenish the concentration of metal ions within the diffusion layer at the cathode, and do the same for negative ions in the analagous layer at the anode. When the current is then switched back on again, the cell can operate with better than average efficiency, reduced stress, and possibly higher than normal plating rates can be achieved even after the current 'off'-time has been accounted for.

The application of a pulsed current(P.C) has shown that due to the surplus of electrical measures/parameters present, the mechanical properties of some materials could be particularly influenced. This particularly important parameter is known as the 'off' or 'dead'time and when the current is off, desorption phenomena will take place.

Desorption is defined as ions may break away from the metal surface and move off into the solution and new atoms may then ionise to replace the desorbed ions. Due to the desorption of decomposition products of salts, the metal density, the ductility, in certain cases even hardness increases and the tendency to produce porosity is reduced.

In pulse plating it is possible to control four parameters which will depend on the equipment used. Figures 1-2 illustrate these parameters and are followed as;(13-14)

- (1) width,(on-time), the length of individual pulses.
- (2) delay,(off-time), the length of time between individual pulses.
- (3) frequency, the number of pulses of electricity and it can be expressed as;

$$F(\text{frequency})=1/(\text{on time} + \text{off time})$$

- (4) current density, the amount of current per square centimeter supplied to the cell during each pulse.

2.3 ORIGINS AND DEVELOPMENTS OF ELECTROPLATING⁽¹⁵⁻²³⁾

2.3.1 HISTORICAL ORIGINS

Electroplating is an application of electrodeposition to produce, coherent, adherent coating of solid metal, and is one of important methods for producing coatings. Faraday discovered electromagnetic induction in 1831 and Pixii used the commutator in 1832 to produce a direct current generator, but it was not until about 1870 that several independent investors used electromagnetic

field coils to generate the heavy currents needed for electrolysis. The production of electricity by metallic corrosion in 1786 was followed by the reduction of metal ions to metal by electrons at a metal/solution interface. Bugnatelli⁽¹⁶⁾ published an account of silver ions as early as 1805.

2.3.2 APPLICATIONS OF ELECTROPLATING

Electroplating is the process of depositing a coating having a desirable form by means of electrolysis. Its purpose is generally to alter the characteristics of a surface so as to provide improved appearance, ability to withstand corrosive agents, resistance.

The most potential industrial application of pulsed deposition is in the process of alloy plating and electroforming from simple ion solutions without the use of complexing agents.

Pulse plating is currently being used in gold plating with the great deal of success⁽²⁴⁻²⁶⁾. This method gives a finer grained deposit and better electrical conductivity. This mode can produce fine-grained electrodeposits with better part to part distribution at as good or better than normal plating rates.

Electrodeposited nickel is typical of metals which can be included in the above category. It is often applied for decorative and protective purposes. Most nickel coatings in form of this, corrosion resistant and often also decorative coatings are chromium plated to form the familiar

composite nickel pulse chromium system. While nickel coatings may be applied solely for corrosion resistance where their inherent dullness is of no importance.

Gold electroplating processes have many important industrial. An application particularly important, especially in recent years, is the application of gold plating processes to the manufacture of electronic circuits. Because of its electrical conductivity properties and the fact that it does not form a surface insulating layer, gold is especially useful as a conductor in electrical circuits as well as a surface metal in electrical contacting areas. Because of the extensive use of gold in electrical circuit as well as its high cost, it is advantageous to conserve as much as possible the amount of gold used in a particular application without sacrificing the quality of the electronic circuits.

Certain metallic substrates are traditionally difficult to plate with an adherent metal coating, for example; aluminum and aluminum alloys are characterized by numerous plating difficulties, including problems of adhesion of metal coatings. A solution to the problems inherent in plating aluminum is especially important due to present day needs for light weight vehicles.

2.3.3 ELECTROFORMING

Electroforming is quite similar to electroplating (ie using the basic particles and equipment) except that instead of coating an article in electroplating, the article is manufactured or reproduced on to a

mandrel⁽²⁶⁻²⁹⁾. The process of electroforming follows that⁽³⁰⁾, metal ions by electro chemical are transferred through an electrolyte from anode to a surface of plated metal.

Most types of electroforming use nickel because it is tough and strong⁽²⁷⁻³¹⁾ and it is also highly resistance to erosion, abrasion and corrosive attack. The hardness of electrodeposited nickel varied between 150 and 600 Hv.

In order to lower the deposit stress, sulphur can be used but unfortunately it induces an embrittlement in deposits⁽³³⁾. It is essential to ensure that internal stress in the deposit is zero, hence addition of organic stress reducing agent should be used in Watts solution whereas in sulphamate^(30,34-36) solution this stress can be reduced to zero at lower temperature (60°C). The hardness can be varied between 150-450 Hv.

According to Watson and Worn⁽³⁴⁾, Ni speed is a most suitable process which has been developed by Inco to reduce the limitations of electroplating. This process does not involve the organic stress reducer and can be used at high current densities.

Electroforming has a wide range of application such as gramophone record production, printing applications^(37,27), mould and dies, mesh products, foundry patterns, press tool^(34,36,38) or tools for texturing and leather grain-ing, electronic applications⁽³⁹⁾, Jewelry items.

Wearmouth⁽³²⁾ has shown that cobalt or nickel deposits would be ideal for dies and moulds and with lower cobalt in solution and lower current density, a lower stress will result, but with increase in current density will reduce the deposit hardness.

2.3.4 NICKEL-IRON ALLOYS

Pulse plating of nickel-iron alloys has received considerable attention. Avila and Brown⁽⁴⁰⁾ found that, with pulsing, the alloy composition was much closer to the solution composition, and was also independent of the thickness of the deposit. Beltowska-lehman⁽⁴¹⁾ investigated the effect of pulsing on the internal stress of thin permalloy films, (80Ni-20Fe) in order to control the magnetic properties. He found that pulsing, in fact, produced higher stress levels, particularly at higher frequencies (500Hz) where the crystallite size was smaller. Nishizawa⁽⁴²⁾ found that pulsing resulted in permalloy films that were bright and had a fine grain size. The current efficiency, particularly for iron, was greatly improved and necessitated reducing the concentration of ferrous ions by one third compared with D.C plating.

Recent papers by Maksimovic⁽⁴³⁾ have shown that the electrodeposition of Ni-Fe alloys had a variable composition when they were electroplated by a constant or pulsating potential. He used a constant potential and proved that the $[Ni]/[Fe]$ ratio in the alloy depended upon the ap-

plied potential for current densities lower than the limiting current density. Simultaneously, experiments with a pulsating potential enabled a reduced iron content in the alloy to be obtained either with increase in amplitude or reduction in frequency for the same average potential value. Other advantages include wider current density range for alloy plating. Faster coverage on molybdenum or tungsten surfaces and fifty microinches of pulse plated Gold seems to have the same corrosion resistance as 100 microinches of D.C plated Gold deposits.

The use of pulsed current is quite well known as a research tool for studying the electrodeposition mechanism of metals. With increasing emphasis on the properties of the deposits, it is therefore realised that this method of deposition could well provide a means of improving their properties. However, the good metal deposits are⁽⁴⁴⁾ produced by pulse plating in the frequency range of 10-500 Hz.

Ibl et al⁽⁴⁵⁾ have shown that, with using short pulses of large current amplitude followed by a relaxation time adequately long to allow complete relaxation of the diffusion layer, good quality deposits can be obtained. Also Gurovich and Krivtsov⁽⁴⁶⁾ have shown that increasing pause - to pulse ratio will result in a decrease in the surface roughness of metal deposits.

According to Viswan and Raub⁽²⁴⁾, with short current pulses and longer 'off' times, no significant diffusion

polarisation occurs during plating.

The other techniques include the effect of superimosing an a.c on d.c on the electrodeposition of Co-Ni alloys from a Watts⁽⁴⁷⁾. Also with higher frequencies, the capacitance current of the periodic charging and discharging of the double layer produces a smearing⁽⁴⁸⁾ effect of the Faradaic current wave as if the frequency though the overall current appears to be pulsating. However, lowered stress due to off period allows the mass transport to fill up depleted ionic concentration within the cathode diffusion layer, enabling the cell to utilise its current at increased efficiency when the power is switched on again.

Ll carnini and Ib⁽⁴⁹⁾ has reported that with pH=9 and high current density, it is possible to produce palladium coatings of 5 μm thickness without cracks and porosity. As the current density (c.d) increases, the hardness and number of cracks decreases.

Hayashi, Kitanishi and Fwkumoto⁽⁵⁰⁾ have shown the effect of 'off-time' [T] increases, with the duty cycle in the following order of 1/25 to 1/250, formation was favoured of granular growth to the block type deposits with the constant current ($50\text{A}/\text{dm}^2$) and T(0.5 or 1ms). Using X-ray diffraction analysis, it was found that with lower current density range ($0.5\text{-}1\text{A}/\text{dm}^2$), the domain size is greater than 5000\AA and there is rather high stress in the deposits in the case of silver-ammonia bath. However, with silver deposits in cyanide bath, small domain size of about 3000\AA and low internal stress in deposits will

result.

Popov, Maksinovic and Stevanovic⁽⁵¹⁾ have reported that with increasing pause - to pulse ratio in pulsating current deposition leads to a decrease in the size and increase in the number of growing grains.

Raub and Knodler⁽²⁶⁾ have reported that with polymer formation in deposits of hard gold, the nickel and cobalt content are increased and at the same time reduces the oxygen, carbon and nitrogen/hydrogen contents. High bright deposits can result from high nickel but low polymer concentration.

2.3.5 PULSE PLATING OF Ni ALLOYS

The most recent papers which presented by Cherkaoui et al⁽⁵²⁾ has demonstrated that pulse plating of Ni-Cu alloys, using 50-100Hz and pulse current density of 20-25 A dm⁻², has produced smooth and bright deposits with 30Wt.% Cu. The roughness was considerably reduced and brightness much enhanced as compared with d.c. plated alloys of the same composition.

Pulse plating of electrolytic copper was also investigated by Montgomery⁽⁵³⁾. He carefully described that with positive and negative pulsing conditions the resistance and other relevant mechanisms could be influenced to improve the performance relative to DC.

Pearson⁽⁵⁴⁾ has shown the effect of pulsed current on the properties of electrodeposited chromium. He managed to reduce the internal stress of chromium deposited in sulphate-catalyzed baths and reduced or eliminated cracking.

Pulsed current electroplating of silver-gallium alloy was investigated by Reksc et al⁽⁵⁵⁾. They showed that the codeposition of 4.0 to 4.5% gallium has increased the hardness of silver and improve wear resistance fourfold with only an insignificant increase in electrical resistivity.

Current distribution in selective pulse plating was shown by Chin et al⁽⁵⁶⁾. A mathematical model was represented for the distribution of the time averaged local current density on a large unmasked cathode, the cathode surface was facing a small rectangular anode in plating cell. Numerical computations were made for the pulse plating of gold from a concentrated neutral phosphate gold bath and copper from an acid copper sulphate bath.

Current pulses at 200 to 400 mA/cm² with an on-time of 0.1 msec and an average current density of 4.0 mA/cm² were the optimum pulsing conditions for Shan-Jiang⁽⁵⁷⁾ to deposit bright, smooth silver alloy containing about 25% palladium. Deposit composition appeared to be controlled by diffusion polarization.

A study of the current efficiency decrease accompanying short pulse time for pulse plating was carried out by Chen⁽⁵⁸⁾. He demonstrated that when the on-time was shorter than a critical pulse time, the efficiency dropped noticeably.

The theory of Saccharine additive was carried out by Beltowska-Lehman⁽⁴¹⁾. It was found that the Saccharine effect reaction was diffusion controlled. This was shown with an experiment involving 0.6g Saccharine on the kinet-

ics of Ni-Fe-Co deposition . The reduction of Saccharine on the cathode causes easier hydrogen evolution. Hydrogen reduction rate increases as the intensity of agitation increases, this corresponds to the Saccharine reduction reaction being diffusion controlled.

2.4 MECHANISM OF GENERAL ELECTRODEPOSITION

Much effort has been given in recent years to studying the mechanism of electrodeposition. Most investigators⁽⁵⁹⁾ have assumed that electrodeposition should follow a mechanism akin to that for the deposition of a crystalline coating by condensation of a vapour. The solvated metal ion approaches and adsorbs on the cathode, losing some of its solvation sheath as the cathode gains the requisite electrons. The ad-ion which is mobile, diffuses over the cathode surface until it reaches an atomic step. It adsorbs on the step, losing more water of solvation, and reducing its freedom to diffuse along the step. Further desolvation and co-ordination follows when it reaches a kink in the step, at which stage it is mobilised. When other ad-ions following this path eventually join and submerge the first, co-ordination occurs with metal ions in the metallic lattice. The view of Capuano et al⁽⁵⁹⁾ was that the mechanism of electrodeposition was plausible, compatible and consistent with later views on metallic crystals and their defects, and certain properties of electrodeposits.

The actual process of deposition is as follows (10-12)
Salts consist of ions that have negative or positive

charges, and migration of these ions in the solution constitutes a flow of electricity. Salts are electrolytes; they conduct electricity, not only in solution, but also in molten state. Such electrolytes are decomposed in the process called electrolysis, in which electrical energy becomes chemical energy. But chemical energy can also be converted to electrical energy.

A simple cell shown in fig 3 may be used to illustrate the mechanism involved. The potential difference across the cell due to the current source makes an excess of electrons available at the cathode as it becomes more negative than the anode. This potential attracts positive ions in the solution to the cathode where they are neutralised either by free electrons in the lattice, or by ions accepting electrons and hence becoming incorporated into the lattice at the cathode surface. Whichever process by which the positive ions become neutralised at the cathode, electrons are required from the external circuit. Therefore, as positive ions are deposited at the cathode, then current must be supplied to the cell. Reduction of metal ions by addition of electrons at the cathode must be accompanied by an oxidation process, loss of electrons at the anode. The latter process generally involves the removal of electrons from the metal into the external circuit. This leads to the loosening of metal ions at the anode surface due to the reduced binding forces. These metal ions may then form a hydrated ion by combining with a water molecule in order to facilitate effective trans-

port of metal ions through the solution. This hydrated ion in the solution is then attracted to the cathode and becomes incorporated in the cathode lattice as it separates from the water molecule which stays in the plating solution and can then contribute to further metal ion transport. The anodic and cathodic processes are necessarily self-regulating and occur on average at the same rate, simply because the cell potential governed by the external power supply is common to both electrodes.

Any difference in reaction rates at either electrode leads to a change in the potential which slows down the reaction rate at whichever electrode is involved, speeding up the reaction rate at the other in order to equalise the rates.

However, other investigators⁽⁶⁰⁻⁶¹⁾ have a more detailed approach than shown by the previous model. They indicate that under the influence of an imposed electrical field as well as by diffusion and convection, the hydrated metal ion present in the electrolyte arrives at the cathode. The hydrated metal ion enters the diffusion layer in which the migration velocity is determined by the concentration gradient. The field strength in the diffusion layer is not sufficient to liberate the metal ion from its hydrate envelope. At most, the loosely bound water molecules are aligned by the field. The metal ions then pass through the diffuse part of the double layer and enter the external layer of the fixed double layer. The field strength, (E) in the double layer is approximately 10^7 v/cm, and at this high field strength the metal ion is deprived of its hydrate envelope. As shown in fig 4 the repelled water

dipoles become components of the double layer.

Brandes, Erdey-Gruz and Volmer⁽⁶²⁻⁶⁴⁾ have mentioned that the dehydrated metal ion migrates within the outer zone of the double layer to a point opposite an energetically favourable growth point on the cathode surface. From this point the metal ion passes through the double layer, is neutralized, and deposited on the cathode. According to Kohlschutter⁽⁶⁵⁾, the metal ion passes through the double layer at the point where contact first occurs. It is then neutralized and adsorbed for the time being at the cathode surface as an ad-atom. This ad-atom now diffuses on the cathode to a growth point and is there incorporated into the crystal lattice of the cathode. Only when the first contact chances to be at the site of a growth point of a crystallite can it immediately be built into the crystal lattice.

2.4.1 MECHANISM OF ALLOY DEPOSITION

The principal factors that determine if two metals can be codeposited from an aqueous solution and the ratio of the metals in the resultant deposit produced at any given temperature and current density are as follows;

1. The static or equilibrium potential of each metal in that type of bath
2. The cathode polarization of each metal in the presence of the other, the cathode polarization existing during codeposition
3. The concentration of each metal and of its ions in the solution used and especially in the cathode film

4. The solution potential, the dissolving tendency of the alloy deposit that is or may be formed

5. The hydrogen overvoltage on the resultant cathode alloy surface.

In addition, the results will be influenced by the effects of temperature and current density upon each of above properties. Even though the direction of the effect of each single variable can often be predicted, it is not yet possible to estimate the magnitude of such changes, especially if two or more conditions are simultaneously varied.

Fig 5 shows three typical cases for two simultaneously deposited cations A and B. In fig 5A, the two cathode potential-partial current density curves are far apart. During electrolysis the cathode assumes the discharge potential of the more noble metal. The cathode process consists of the discharge potential of the more noble metal. The cathode process discharges the cations of metal A and the deposition potential of the metal B is not attained. At the potential E_1 , the limit current density i_{lim} of the more noble cation is attained. The potential E_1 then becomes suddenly less noble until discharge of the cation B begins as the second reaction. With further increase in current density, cation B is increasingly discharged, while deposition of the metal A remains the same on an absolute scale but decreases on a percentage scale.

Fig 5B. represents the two cathode-current density curves

which are close to each other. The deposition potential of the less noble metal is attained even at relatively low current densities. Thus, codeposition of B is possible before the limit current density of A is achieved. At the potential E_1 , the corresponding partial current densities are $i_{A,1}$ and $i_{B,1}$ and at the potential E_2 , $i_{A,2}$ and $i_{B,2}$. The conditions for the simultaneous deposition of two metals are most favourable when the cathode potential-current density curves are identical. This case, however, can hardly be realized in practice.

Fig 5C. illustrates two intersecting cathode potential - partial current density curves. At the potential E_1 the partial current densities are $i_{A,1}$ and $i_{B,1}$ ($i_{A,1} > i_{B,1}$). At the potential E_2 the partial current densities are equal and thus the current efficiency for both A and B is 50%. At the potential E_3 the partial current density is $i_{B,3} > i_{A,3}$. With such a curve trend, the partial current density i_B increases more rapidly with increasing current density than does i_A . This means that the current efficiency decreases with respect to the cation A. In practice, various values for the current efficiency may be found depending on the relative positions of the cathode potential partial current density curves.

The presence of complex ions⁽⁶⁶⁾ is also very important when alloy deposition is considered. For example, brass plating from cyanide solution is achieved by the discharge of $\text{Cu}(\text{CN})^{3-}$ and $\text{Zn}(\text{OH})^{2-}$ (rather than $\text{Zn}(\text{CN})^{2-}$) ions. The reversible electrode potentials of copper and zinc in acid

solutions of unit activity are +0.34V and -0.76V respectively and the corresponding potential-current density curves are shown in fig 6.

Fig 6A. shows clearly that there is no potential which could be applied at which both metals could be simultaneously deposited from these acid solutions. All the copper would be deposited first and then the zinc. The effect on the E-i curves using the cyanide solution is shown in fig 6B. Thus, simultaneous co-deposition is now possible. The reason for this behaviour is that the formation of complexes reduces the activity of copper ions to about 10^{-18} g ions/l although the concentration of copper in solution is about 1 mol/l. The copper ion is Cu^+ in the complex and E for this ion is +0.55V. The zinc complex ion is relatively weak but the activity of Zn^{2+} ions in solution is not as markedly affected.

The simplest nickel-iron plating baths⁽⁶⁷⁻⁷⁶⁾ are based on the sulphates, chlorides or sulphates and chlorides of the two metals. Stabilizers or complexing agents are often used to diminish the formation of insoluble ferric hydroxide, ie Fe^{+3} and organic hydroxy carboxylic acids are satisfactory.

Generally, metals having standard electrode potentials (E°) that differ by less than 0.2V can be codeposited. Potential (E) of a metal immersed in a solution of its own ions depends upon the standard electrode potential and the activity of the ions (a), as related by the Nernst equation;

$$E = E^{\circ} + (RT/ZF) \log_e a$$

where;

R= gas constant = 8.31

T= absolute temperature =298 K

Z= valency of the reacting ions

F= Faraday constant =96500 Coulomb

The discharge potential for deposition also depends upon the over-potential η and is given by;

$$E_{\text{dis}} = E^{\circ} + (RT/ZF) \log_e a - \eta$$

Hence for two metals to simultaneously deposit, their potentials must be equal, so;

$$\begin{aligned} E^{\circ} + (RT/ZF) \log_e a - \eta &= E^{\circ} + (RT/ZF) \log_e a - \eta \\ E^{\circ} + (RT/ZF) \log_e a - \eta &= E^{\circ} + (RT/ZF) \log_e a - \eta \end{aligned}$$

For the iron-group metals the standard electrode potential are -0.250 V for nickel, -0.440 V for iron.

2.5 ELECTRODE POTENTIALS

An aqueous electrolyte solution consists of a variety of charged and uncharged species as follows;

- (1) cations, which are positively charged ion and migrate to the cathode in a galvanic or voltaic cell,
- (2) anions, which are negatively charged ion; they migrate to the anode a galvanic or voltaic cell,

(3)water dipoles,

(4)organic molecules, trace impurities which under equilibrium conditions are randomly oriented so that within the solution there is no preferentially directed field. Under the influence of a potential difference, the charge will be transported through the solution by cations and anions that migrate to cathode and anode, respectively; this migration of charge is through an electrolyte for electrolytic conduction. At each electrode there will be a transfer of electrical charge and a consequent electrode reaction that results in a change in the concentration of the reacting species at the surface of the electrode. Under these circumstances the transport of species to and from the electrodes is by diffusion and convection as well as migration; the term 'transport' is used to include diffusion, convection and migration. Fig 7 shows the potential differences and concentration gradients in the cell $Cu/NiSO_4/Cu$. Fig 7a. represents the electrodes being unpolarised; the potential difference is the equilibrium potential $E_{e,q}$ and there is no concentration gradient in the diffusion layer. Whereas, in fig 7b. the electrodes are polarised; E_p of the anode is now more positive than E_{eq} whilst E_p of the cathode is more negative and concentration gradients exist across the diffusion layer; C_e, C_b are the concentration at the electrode and in the bulk solution. Conversely, the solution deposits ions on the metal and are incorporated into the metal lattice. Because the ions are at the same time charge-carriers, this passage of ions creates "an electrical double" layer at the metal-solution interface.

An electrical double layer(E.D.L) and also known as the (Helmholtz double layer) is the combination of the positive "adsorbed fixed layer" outside and the negative ions diffuse from it to form a "diffuse mobile layer" shown in fig 8. These layers are loosely held there by electrostatic attraction. The potential between the layers is a result of the equilibrium of the chemical and electrical forces. The potential difference which exists between metal and solution in the equilibrium state is known as the galvanic potential. This electrochemical equilibrium is dynamic, so that in the equilibrium state the interaction between metal and electrolyte does not cease although in a given interval of time the number of ions entering the solution from the metal is equal to the number of ions deposited on the metal from the solution. Nernst termed the tendency of the metal to send ions into solution the electrolytic solution pressure and the tendency of the solution to be diluted by depositing ions on the metal, the "osmotic pressure" of the ions.

The galvanic potential existing at the metal-solution interface as a result of the various tendencies of the ions to pass into solution or, alternatively into the metallic state, is manifested at the phase boundry in the form of the electrical double layer. According to Nernst and Helmholtz, this E.D.L must be visualized as consisting of a small but still measurable number of excess positive cations confronting an equal number of negatively charged anions at the interface. When metal ions are tranferred

from solution into the metal lattice, the metal is at the positive side of the E.D.L, opposed to which is the negative side in the adjacent solution layer. When ions escape from the metal and enter the solution, the metal ion is at the negative side of the double layer and the adjacent solution layer at the positive side. The magnitude of the galvanic potential depends upon which of those processes predominates.

A simple mode of the (E.D.L) was suggested by Helmholtz in which the changes at the interface were regarded as the two plates constituting a parallel plate capacitor, eg, a plate of metal with excess electrons (the inner Helmholtz plane- I.H.P) and a plate of excess positively charged ions (the outer Helmholtz plane-O.H.P) in the solution adjacent to the metal. The changes at the interface balance one another so that the E.D.L is neutral as a whole. Fig.8A shows the E.D.L to consist of a plate of excess negative charges on the surface of the metal.

2.6 ELECTROLYTIC CRYSTALLIZATION

The final step which takes place during the electrodeposition of a metal at the cathode is known as electro-crystallization ie, the transition of the discharged metal atoms into the crystalline state.

In electro-crystallization, which proceeds under the simultaneous influence of lattice forces and electrostatic forces, two types of crystal growth are possible. These types are firstly crystal growth starting at edges and

corners, where the highest current densities are present and secondly, at the centres of the crystal planes. The type of growth which predominates depends on the minimum crystallization energy.

According to Kossel⁽⁷⁷⁾, the energy required for continuation of the growth of a given crystal lattice is least where the newly arrived atom can be built into an unfinished lattice plane. Owing to the minimal energy requirement for crystallization at these points, this partial step is repeated many times. Crystal growth thus proceeds by "repeatable" steps called "half-crystal" positions and also called "active" and "growth areas" by Fisher and Lorenz⁽⁷⁸⁻⁷⁹⁾. The forces of attraction in the interior of a metal are compensated by the neighbouring atoms. However, At the surfaces, this is no longer true, and they thus exert growth in the vicinity of the surface. Therefore, these growths are strongest at corners and edges projecting from the surface⁽⁶²⁾. At the growth areas crystallization proceeds in such a manner that one ad-atom at a time is built into the crystal lattice in the immediate vicinity of an atom previously incorporated into the lattice.

In addition to the lattice forces, electrostatic forces also play apart in electro-crystallization. Furthermore, it is necessary to take into a account the fact that the metal ions in electro-crystallization, in contrast to other crystallization processes, are always surrounded by foreign cations, anions, neutral molecules and other

2.7 NICKEL PLATING SOLUTIONS

Commercial nickel plating started about 60 years ago, and for around 30 of those years the 'WATTS NICKEL' solution has dominated the field. This solution is based upon Nickel sulphate to provide the necessary ions, with chloride to aid anode dissolution and boric acid to act as a buffer. In 1938, the first large scale competitor to the WATTS solution emerged. This was the first of the sulphamate solutions and was developed by Cambi and Piontelli⁽⁸⁰⁾. It was some years until the sulphamate solution became commercially viable, but in 1950, Barret⁽⁸¹⁾ introduced the process into the American electroplating industry.

During the 1950's much work was carried to research and develop commercial sulphamate solutions such as by Diggin⁽⁸²⁾ in the U.S.A, Chaetal⁽⁸³⁾ in India and Fanner and Hammond⁽⁸⁴⁾ in the U.K.

The development by Kendrick⁽⁸⁵⁾ of the concentrated nickel sulphamate bath in 1964 led to the patenting of the 'NI-SPEED PROCESS' by international Nickel limited. The importance of this development over the well-established WATTS solution is that the concentrated sulphamate bath allows very high plating rates to be achieved whilst still retaining good mechanical properties and the control of internal stresses.

2.7.1 WATTS NICKEL PLATING SOLUTION⁽¹¹⁾

The basic constituents of this bath are;

- (a) Nickel sulphate.
- (b) Nickel chloride.

(c) Boric acid.

Other additions such as; Wetting agents, Anti-pitting agents and brighteners may be added.

(a) Nickel sulphate provides the majority of the nickel ions necessary and is used because it is relatively cheap compared with other Nickel salts, is readily water soluble and produces a stable anion which is not volatilized, reduced at the cathode or oxidised at the anode. By increasing the nickel sulphate concentration of the Watts solution and increasing the current density (C.D) of the bath, the plating rate can be increased and plate distribution improved.

(b) Nickel chloride functions to provide of the chloride ions chiefly to improve anode dissolution by reducing polarization which prevents passivation. Its presence also decreases the bath resistivity and improves its efficiency and throwing power.

(c) Boric acid acts as a buffer to control the pH of the solution in the cathode film, and its absence may lead to hard, cracked and pitted deposits as shown by Macnaughtan⁽⁸⁶⁾. It therefore serves to promote the production of a smoother, whiter deposit and is a readily soluble, (improved at elevated temperature), readily available and inexpensive addition.

2.7.2 BATH COMPOSITION AND OPERATING CONDITIONS

The main operating variables for the Nickel plating solution are (a) pH range, (b) temperature range and (c) composition and cathode current density.

(a) pH RANGE

The normal operating range of pH is between 1.5 and 4.5. The higher pH tends to increase stress and the deleterious effects such as; impurities on deposit properties can become marked above pH=5. Low pH may allow the cathode current density range to be increased, but it has been found⁽⁸⁷⁾ that the optimum range for best deposit properties and operating efficiency is around 3.0-4.0.

(b) TEMPERATURE RANGE

The accepted operating range is between 45⁰C and 65⁰C within this range, the effects of ion mass transport by diffusion are increased. Temperatures below this range reduce the above effects and temperatures above this range may be impractical as they could be expensive to maintain on a large commercial scale.

(c) COMPOSITION;

A typical composition⁽¹¹⁾ would be;-

Nickel sulphate	:	330 g/l
Nickel chloride	:	45 g/l
Boric acid	:	38 g/l

The nickel sulphate concentration may be increased to say, 400 g/l if higher plating rates are required. Above about 40 g/l, the boric acid has little added effect, and

nickel chloride concentrations above 50 g/l also are unimportant.

(d) CATHODE CURRENT DENSITY

A typical range⁽¹¹⁾ for the composition given is 25-100mAcm⁻². Low current densities may produce bright brittle deposits. intermediate current densities ,(say 50 mAcm⁻²), give a smooth, ductile well adhered deposit. Whereas at the highest current densities, powdery deposits, 'burnt' appearance on leading edges, and eventually high residual stress leading to gross peeling will occur.

2.7.3 THE NICKEL - IRON PLATING⁽⁸⁶⁻⁹⁷⁾

The attraction of nickel-iron plating process is related to evidential metal cost savings which can be achieved. Clauss⁽⁹⁴⁾ mentioned that this cost saving is due to the cost of iron being about 8% of the nickel.

The plating utilities and advantages of Ni/Fe plating include;

(i) The Ni/Fe replates much superior than frequent/normal Ni and covering power is excellent.

(ii) Inferior and reject parts can be run through again without uncovering/stripping.

(iii) The most main economic advantage over Ni plating is that iron is so much cheaper than nickel metal and this will be particularly important if the cost of nickel continues to rise.

(iv) Saving of Ni metal costs according to the company Delwood Furniture⁽⁹¹⁾ is in order of 20-25%, and they use a third of iron anodes in solution.

(v) The amount of of Ni waste is noticeable and can be recycled.

(vi) Operating parameters, such as pH , temperature, current density, voltage, agitation, deposit itself may be used to give more resistance than Ni to burning at very high current densities.

2.8 THE ORIGINS OF RESIDUAL STRESS IN ELECTRODEPOSITS⁽⁹⁸⁾

Owing to the complex nature of electrodeposition and the large number of interrelated variables involved with the plating process, there is no single overall theory covering the causes of residual macrostress. There are, however, a number of theories, reviewed very well by Weil⁽⁹⁸⁾ and the one point upon which they are in general agreement is that macrostress is due to one layer of electrodeposited atoms fitting the one beneath it and subsequently shrinking or expanding, or the layer of atoms is deposited in such a way that it has to be either in compression or tension in order to fit.

The theories proposed to explain these conditions are:-

1. The crystallite - joining theories.
2. The hydrogen theories.
3. Changes in foreign substances theories.
4. Excess energy theories.
5. Lattice-defect theories.

2.8.1 THE CRYSTALLITE - JOINING THEORIES

The basis for this theory overall is that crystalline material growing outward from several nuclei on the deposit surface is pulled together upon meeting, this causing stress. This was first postulated in 1918 by Kohlschutter⁽⁶⁵⁾ et al. Further work was carried out by the latter and his associates, resulting in the theory that the deposit forms initially at isolated sites, (i.e, is highly dispersed), due to hydrogen. The dispersed particles are said to be of high energy, this providing the driving force for recrystallization.

Fedot'ev⁽⁹⁹⁻¹⁰⁰⁾ et al put forward similar theories in 1959 and 1966, adding that the resulting volume decrease upon recrystallization, (to a more dense state), would produce a tensile stress. Thus, stress-reducing additions could fill the intercrystalline spaces prior to recrystallization more effectively than other foreign substances, thereby impeding or preventing the volume change and the resultant residual stress. Some doubt, however, has been cast upon the recrystallization of an aggregate of small grains causing macrostress, since firstly this theory cannot explain how compressive stresses develop, and secondly, high macrostress deposits are generally columnar grained - there being no evidence that they formed initially as fine grains.

It has been observed by, for example Brenner and Senderoff⁽¹⁰¹⁾ that as the substrate grain size increased, so residual stress in the deposit upon the substrate decreased. Under conditions of epitaxy, the larger the substrate grains then the smaller the number of deposit nuclei leading to less coalescence and a lower residual stress value. Still considering the substrate, it has been observed that a stiff substrate can give rise to a higher tensile stress in the deposit than a softer substrate. This is thought to be due to a stiff substrates ability to resist bending under the forces exerted by the stress in the deposit when coalescence occurs⁽¹⁰²⁾. The effects of foreign substances on stress when considering coalescence of crystallites can be similar to those for recrystalliza-

tion since the latter and former are difficult to distinguish. For instance, tensile stress may be decreased by filling the gaps between joining crystallites thus impeding their coalescence - the same idea as with recrystallization. Other effects include the changing of preferred orientation of crystallites due to the foreign substances leading to a greater degree of misfit upon coalescence which will give higher residual macrostress. Also, the attractive forces between crystallites may be altered by impurities which may lead to variations in internal stress.

Many observations have been made where, as the current density rises, so the residual macrostress rises^(85,103-106). This could be due to increased nucleation rate caused by an increase in the overpotential, leading to more joining crystallites. The effect of impurities could provide exceptions to this behaviour due to their reaction to the overpotential.

Plating bath temperature increase is usually associated with a resulting decrease in stress at low current densities, possibly due to higher diffusion rates giving rise to less unfilled space between crystallites upon coalescence - less stress. At higher current densities, the plating and therefore crystallite growth rate are possibly too high for the effects of increased diffusion at higher temperature to make any difference to the stress. Certain effects of pH on stress can also be explained in terms of impurity behaviour.

The electrodeposition process is generally one of the continuous growth or 'flow' of single or multi-atom layers over the crystal layer beneath. In the absence of impurities and with single crystal deposits, the edges of such growing layers should be smooth leading to the joining of crystallites without misfit and therefore without stress. This has been proved experimentally by Schneider and Weil⁽¹⁰⁷⁾ using a purified electrolyte. In the presence of impurities acting as growth inhibitors, however, the growth layers do not have smooth edges, leading to the joining crystallites touching at irregularities protruding from the growth layer first, leading to premature coalescence, (as if two liquid drops were meeting), and the pulling in of the crystallites forming stress. The effect of stress reducing additions could be to fill in the gaps or steps around irregularities thus promoting a smoother growth edge around crystallites, thus delaying coalescence so that when the crystallites do join they do not have so far to move upon coalescence, leading to lower stress.

2.8.2 HYDROGEN THEORIES

This assumes that a layer of deposit contains hydrogen which may combine with the metal deposit to form a hydride. The hydride then is assumed to decompose leading to a decrease in volume, and the outward diffusion of hydrogen. The substrate and deposit layers beneath this shrinking layer resist the contraction, and a tensile stress is caused.

Compressive stresses result if the hydrogen diffuses to favoured sites such as dislocations and vacancies and

forms gas pockets. This is a similar effect to hydrogen embrittlement, and the high pressure inside these pockets could lead to an expansion of the deposit and a resultant compressive stress in that layer.

Some evidence for the validity of this theory is that a strip bent in a way indicative of a tensile stress in a deposit can be straightened by hydrogen charging according to Hothersall⁽¹⁰⁸⁾.

The stress minimum observed at some intermediate current density of certain nickel deposits can be explained in terms of the hydrogen theory. The limiting current density for hydrogen deposition could be reached below the intermediate value of current density where the stress minimum has been observed. Thus, at lower current densities there would be more hydrogen to enter and cause stress in the deposit.

The interaction between hydrogen and foreign substances is not clear, but it is thought that certain impurities may combine with hydrogen and prevent any volume decrease in the deposit, leading to a decrease in stress. Conversely, impurities could provide sites for hydrogen to form gas pockets and give an increased residual stress.

In some instances, the hydrogen theory has been combined with other theories. Kohlschutter⁽¹⁰⁹⁾ stated that hydrogen was the major cause of the isolated crystallite deposit nuclei which represented a state of excess energy. Hydrogen evolution is generally accompanied by a rise in the pH in the vicinity of the cathode which can, in turn, result in the formation of new foreign species. It must be noted that hydrogen is definitely not the only cause of

stress in deposits, as stresses have been observed when there was no hydrogen codeposition⁽¹¹⁰⁾.

2.8.3 CHANGES IN FOREIGN SUBSTANCES THEORIES

Alterations in the shape, orientation or chemical composition have been postulated to cause the volume change of a plated layer relative to the one above or beneath it, leading to stress.

The codeposition of foreign substances does not, according to Popereka⁽¹¹¹⁾ et al, cause a macrostress as long as their distribution and concentration do not change with thickness, and the substances themselves do not undergo any changes. The theories involving volume changes due to the decomposition, dehydration or orientation changes of foreign substances do not appear to have adequate experimental support, and must be held in some doubt. The effect of foreign materials on stress can be explained in a more experimentally consistent way by the effect that materials have upon lattice defects such as dislocations and vacancies.

2.8.4 EXCESS-ENERGY THEORIES

The excess-energy theory was first proposed by Barklie and Davies⁽¹¹²⁾ and later by Soderberg and Graham⁽¹¹³⁾ who observed that metals which deposit with a high overvoltage, tend to exhibit high tensile macrostress. Barklie and Davies⁽¹¹²⁾ claimed to have found a linear relationship between macrostress and overpotential, and they assumed that this was related to the storage of potential energy by the elastically stressed lattice.

Later in 1947, Soderberg and Graham⁽¹¹³⁾, postulated that a high overpotential was equivalent to a high temperature at the deposition surface, said to be due to the heat of neutralization of ions upon being incorporated in the lattice at the cathode.

The contraction upon 'cooling' was said to provide the volume change necessary to explain the macrostresses produced.

A later amendment to these theories was made by Gabe and West⁽¹¹⁴⁾ who said that a high effective surface temperature was reached only as far as the number of vacancies which are produced in the deposit. Other workers compared the excess energy due to the overpotential with the stored energy in the stressed deposit and found them to be of similar orders of magnitude. It must be noted, however, that microstresses must also be accounted for in the calculation of stored energy.

Finally, whilst overpotential and macrostress are related in some way, and can be a way of storing energy in the deposit, other factors such as microstress and defects which are also areas of high energy, can not be ignored. The excess-energy theory, therefore is simply another complicating factor in the theory of stress and must be taken into account along with all the other factors.

2.8.5 LATTICE-DEFECTS THEORIES

The majority of the more recent residual stress theories include or are based totally upon the dislocation

theory of metals. The best developed of these is thought⁽¹¹⁵⁾ to be that which explains residual macrostress in terms of the lattice mismatch between deposit and substrate of different metals under conditions of assumed epitaxy, (i.e, the deposit continues the structure of the substrate). The greater this mismatch or misfit between the lattice parameters of the deposit and substrate, then the greater the associated strain energy. This high strain energy can be relaxed by the creation of edge dislocations, (either positive or negative), so long as a reduction in total energy is achieved overall. Thus, at a certain misfit value, it becomes energetically favourable for so-called 'misfit dislocations' to form.

Two dimensional arrays of such dislocations have been observed by Thompson and Lawless⁽¹¹⁶⁻¹¹⁷⁾ in both nickel and gold deposited on copper. There is little doubt, now, as to the existence of these misfit dislocations.

Apart from the lattice mismatch itself, the rate of growth of deposits has an effect upon the development of misfit dislocations. If the growth rate is so fast, (e.g, at high current densities), then the lattice strain energy due to mismatch can not be relaxed quickly enough by dislocation formation and this could lead to the formation of three-dimensional deposit nuclei as a means of energy reduction - this in turn giving a high residual stress.

This lattice defect theory does seem to explain very well the formation of stress in epitaxial deposits, but it is still not clear as to how defects come into play exactly

when the deposit does not take up same structure as the substrate, and other theories have then to be invoked.

However, dislocations in electrodeposited metals are not of the simple edge type, but are complex and often tangled, therefore the mechanism by which dislocations cause internal stress are not quite clear.

In summary, whilst all the other theories of stress must be considered possible, it is obvious that there is no single cause of stress in electrodeposits, but it must be said that some of the theories are more likely than others. By a process of elimination it seems that the dislocations theory or lattice-defect theories are the best overall in explaining the whole range of stress conditions, and the crystallite - joining theories have a sound experimental basis, whereas the experimental links for some of the other theories seem a little tenuous.

2.9 THE MEASUREMENT OF MACROSTRESS

INTRODUCTION

The first records of stress measurement was carried out by Gore⁽¹¹⁸⁾ in 1855 and some twenty years later, Mill⁽¹¹⁹⁾ and Booty⁽¹²⁰⁾ came the first attempt to measure the stresses in electrodeposits. These electrodepositors understood not only the essential nature of the phenomenon but also its damaging action either because the deposit parted from substrate and (and then itself deformed) or because - where the substrate was thin section - the stress resulted in deformation of the whole assembly. Subsequently, other and equally harmful effects related to stress were revealed, including;

(a) The reduction of the fatigue life of components plated with a deposit in tensile stress, even though its adhesion was apparently unaffected.

(b) Enhanced corrosion and corrosion cracking have also been traced back to stressed deposits, not to mention more obvious phenomena such as blistering. From this point, these followed naturally a desire to measure such stress and a number of methods have been devised for this purpose, which will be considered here.

Stress measurement was inevitably difficult because the literature consists not only of descriptions of new methods for stress measurement but also of papers criticizing older or extant techniques.

2.9.1 PRINCIPLES AND PROBLEMS OF STRESS MEASUREMENT

The basic principle of electrodeposit stress measurement is either to measure the deformation of a substrate onto which a metal has been plated or opposed such deformation with a counter-face, which is itself measured.

The weakness in the first of these two approaches is that the deformation which allows stress to be measured, itself relieves that stress and to that extent corrupts the resulting measurement. There is a further subdivision possible in respect of the former category. In some methods, the deformation takes place during the electrodeposition. In others, the substrate is rigidly held and no deformation is possible until completion of the experiment. The constraint is then released where upon the deformation occurs and can be measured.

One may also conveniently divide stressmeters into the following two categories. In the simpler (and less expensive) types, a very thin and easily deformable substrate is used. The imposition of deposit stress on such a substrate, gives rise to large deformations (of the order of several mm) which can be readily measured. The weakness of this approach, as has been stated, is that because the substrate is so pliable, it allows relief of the stress it is intended to measure. This effect limits the accuracy of which such instruments are capable. It also implies, by and large, that stress cannot be continuously measured during a deposition trial and that stress - thickness data can only be built up a tedious succession of experiments.

The more sophisticated stressmeter incorporates a stiffer substrate, whose deformation will therefore be smaller. To compensate for this, some form of "amplification" is therefore included so that the actual measurement may be sufficiently sensitive. Among the methods used to achieve such "amplification" one may list the following;

- (a) Gearing (Brenner-Senderoff)
- (b) Optical lever (Hoor Arrowsmith)
- (c) Electrical amplification(Roch)
- (d) Hydraulic (Kushner)
- (e) Vernier scale (Boeing)

In addition to classifying stress-measuring instruments in the above manner, they may be sub-divide in another way. On the one hand there are those instruments where, because the electrodeposition occurs on one side only of the substrate, there is a deflection. On the other hand, there are those instruments where deposition is allowed to take place on both sides of a strip which is not therefore deflected, but increases or decreases in length. This last approach is known as the "dilatometric" method. The means by which the change in length is recorded may be electrical or mechanical, and will be described later. However by plating on both sides, the need for stopping-off of one side, as required in all spiral designs, is obviated to some advantage. Finally, as will be seen, there are instruments in which no deformation occurs, this being resisted by an opposing force. Such "null" devices avoid almost all possible relief of stress with the resulting

errors.

It was recognised quite early on that the longer the substrate, the greater the deflection, the actual displacement being cumulative. Thus many stressmeter designs are based on spirally-wound substrates (Brenner - Sender-off, Boeing) or long strips (Hoar -Arrowsmith, the IS meter (Dilatometer)).

In comparison of stresses, rather than measurement of absolute values, it is important that similar thickness of deposit are used for comparison. The relationship between deposit thickness and stress is considered below. The immediate implication of this is that, in order to use a stressmeter correctly, a constant current power supply (not constant voltage) should be used, and deposits should be formed at set current values and for known times.

The distribution of the deposit over the surface of the substrate, whether this be a strip or a spiral, must be uniform and this implies either conforming anode geometry or (less satisfactory) large anode - cathode separation. Common errors are the use of spirals which are not insulated on their inside face with the result that while the majority of the deposition takes place (as it should) on the outside face, some will occur on the inner face where it will partially off set the deflection due to stress acting on the outer surface. Boeing equip their spiral contractometer with a cylindrical anode basket in order to give the most uniform deposit distribution over the sur-

face of their spiral.

2.9.2 PROBLEMS ARISING FROM USE OF STOP - OFF MATERIALS

Many designs of stressmeter require that one surface of the cathode be insulated by the use of some stopping - off material or resist, but difficulties arose from the dangers inherent in this, which include;

(a) Contamination of the test solution with species leached out from the resist - which may alter the stress level in electrodeposits.

(b) A swelling of the stop-off layer due to uptake of water leading to a change in stress. (it can be assumed that application of a stop-off layer will itself apply a stress but this, if curing complete, will be taken up in the instrument zeroing procedure.

(c) A contamination, by the stop - off material, of the working surface, as a result of "creep" action.

The use of "permanent" stop - off has largely removed such problems.

2.9.3 EFFECT OF TEMPERATURE CHANGE

Certain operational problems are common to all types of stressmeter. These arise primarily from changes in temperature and in particular, the change in temperature when the instrument is first immersed in the plating bath. Subsequent variations in temperature following the preliminary equilibration can well limit the accuracy of the stress determination. Almost all types of stressmeter are temperature sensitive, albeit for a variety of reasons. One has a bimetallic strip which will have its own

temperature deformation characteristics, it is important to allow the instrument to equilibrate before making a measurement, some instruments (such as the Ismeter or Dilatometer) incorporate a separate adjustment facility for this - usually the range of allowing time for this sort of instrument is 20 - 30 minutes. Change in temperature will affect the sensing element (be a strip or a spiral) and also the framework or support on which it is mounted. One tactic found in several publications, is to make both sensing element and support, of alloys such as Invar, whose temperature coefficient is low. Parallel with this, runs the principle of ensuring that both element and support are made of the same metal, whatever that be, so that differential temperature effects are eliminated. Therefore, the summary of above problems are;

- (i) temperature change on initial immersion
- (ii) subsequent temperature fluctuations in the bath
- (iii) Bimetallic action due to (ii).

To these, a fourth must be added. The passage of a current through any conductor (except a superconductor) causes Ohmic heating. Then too, the energy latent in electrochemical over voltage is also released as heat⁽¹²¹⁾. In short, the electrochemical deposition reaction will, for both of the above reasons, release heat and so cause a temperature rise. These effects must be taken into consideration when seeking to make accurate stress determinations. One approach has been to pass a current through the spiral of the Brenner-Senderoff contractometer from one end to the other, or from end to end of the strip in the IS meter

(Dilatometer), while these are immersed in electrolyte. No electrolysis takes place, the action is simply to use the strip or spiral as a heater element, and the change in length is noted. There is of course a fallacy in this, in that, during electrolysis, the entire current does not pass from end to end. Some travels the whole length, some travels halfway and some enters the strip close to the current take - off point. The second short coming of this method is that it does not measure the heat energy released from over voltage effects. Nevertheless, it offers a means of roughly gauging the magnitude of this effect. Several soviet authors have studied these effects, including PoluKarov et al⁽¹²²⁾.

2.9.4 CALIBRATION OF STRESSMETERS

The simplest and most widely used calibration method is, in a separate experiment, to load the stressmeter mechanically in some way, thereby reproducing the same deflection as was obtained during the electrodeposition. Wherever there is a rotary motion in the instrument, a pulley may be attached (Boeing) or a torque - arm (Koch et al⁽¹²³⁾) and using weights and a string, a known load applied. The Brenner - Senderoff instrument can also be calibrated in this way. Kushner, in his US patent recommends calibration of his instrument by placing a weight on the membrane. One has reservations as to this, since after even a small deformation, the weight would be suspended by an annulus around the gasket and its distribution would be quite different from the stress it is intended to simulate - furthermore - though this might not be a serious objection - deformation of the disc which, under electrochemi-

cal stress may be convex or concave (tensile or compressive) can only be reproduced in the concave sense in this way.

In another description of his instrument⁽¹²⁴⁾ he advocated a calibration procedure based on hydraulic pressure as the device is lowered deeper into the electrolyte solution and this seems to be a far better idea. The Hoar - Arrowsmith machine was calibrated by laying it on its side and placing small weight on the strip. The magnetic force (and required current) to return the strip to the centre position was then noted.

3.0 EXPERIMENTAL METHOD

3.1 GENERAL DESCRIPTION OF THE EQUIPMENTS

Table 1 shows the list of main items used for pulse and conventional-plating.

3.1.1 POWER MOSFETS

The function of Power Mosfets is to offer the superior characteristics of field effect transistors at true high power levels. Power Mosfets simplify circuitry because they are voltage - controlled devices and require only very small instantaneous current from the signal source.

The advantages of Power Mosfets are;

1. They achieve switching times of less than 100 nanoseconds at high current levels.
2. They have great ruggedness because of the absence of the second break down failure mechanism of bipolar transistors.
3. In parallel operation they inherently 'current share' rather than 'current hog'. The stability of the gain and response time characteristics over a wide temperature range is outstanding.

Power Mosfets are majority carrier semi-conductor devices, and their construction and principles of operation are fundamentally different from those of traditional bipolar transistors, which are minority carrier semi-conductors as shown in fig 9.

The terminology used is to referred to drain, gate and source , rather than to collector, base and emitter respectively for a Mosfet and this terminology is compared and shown in fig 9a . Fig 9b shows the voltage must be

applied between the gate and source terminals to produce a flow of current in the drain.

The gate is isolated electrically from the source by a layer of silicon oxide. Theoretically no current flows into the gate when a direct current (D.C) voltage is applied to it - though in practice there will be an extremely small leakage current, in order of nanoamperes.

The extremely low drive current requirement, ie, (input is low but output is high) of the power Mosfet, and the associated extremely high gain are a major advantage over the conventional bipolar transistor. The much lower drive requirement or the Mosfet will usually mean that the vastly superior switching speed will offer the possibility for lower losses current efficiency, or higher operating pulse frequency.

3.1.2 OSCILLOSCOPE

The oscilloscope used was a Farnell type and the function of the oscilloscope is to show the variations in potential on the screen of a cathode ray tube, by means of deflection of a beam of electrons, (ie, variations of current as a weavy line).

3.1.3 POWER SUPPLY

A D.C power supply was used to produce a current up to 10 A. The current stability was determined by means of measuring output variations and this was shown to be effective by following causes;

(a) current instability

- (b) mains supply change
- (c) temperature change in the equipment.

3.1.4 PULSE GENERATOR

The function of pulse generator is to provide a wide range of facilities and operating modes. ie, producing a train of square pulses.

Period is adjustable in seven decade ranges from 100ns(10MHz) to 10(1Hz) and a fine control is provided to give continuous adjustment between ranges.

The output is similarly adjustable from 30mV to 10V into 50 .

The instrument is normally supplied set for operation from an AC mains supply of 198 to 260 volts but can be supplied or adjusted for operation from 95 to 130 volts.

3.1.5 COPPER COULOMETER

The function of copper coulometer is to obtain accuracy of electricity flowing through bath. The standard copper coulometer solution was made for 2.5 litres which contains;

375 g		copper sulphate
67.5 ml	concentrated	sulphuric acid
156.25 ml	concentrated	alcohol

The solution was kept in the beaker with top lid as shown in the fig 10. This solution was used everytime the plating carried out as a standard part of cell.

3.1.6 THE EFCO-METER (DILATOMETER)

An EFCO -meter was used for bath measurement of stress. This meter would provide a continuous measurement of internal stress in metallic coatings during electrolytic or chemical deposition.

It is capable of measuring both tensile and compressive stress of metal coatings to the same accuracy on a range of substrate materials. The metal strip used as a substrate known as shim and the standard length of shim was 25cm long. The use of disposable metal shims for the plated specimen eliminates the lengthy preparatory work necessary with other methods of internal stress measurement.

The principal features of the Efco Internal Stress Meter are shown in fig 11. It consists of a robust p.t.f.e-coated stainless steel frame, in which is mounted a flat, uniform strip of mild steel (working length 200mm, with 10mm end and thickness 0.05mm), pre-tensioned by a spring at its upper end.

3.1.6.1 PRINCIPLE OF OPERATION OF EFCO METER

This is a dilatometric method which relies on the elastic expansion or contraction of a pre-stressed steel strip, brought about by the force developed along its axis by the tensile or compressive stress in the deposit grown on its two surfaces. As both sides of the strip are plated, the theoretical problems of transverse relaxation encountered by some other methods do not arise.

Changes in length of the strip during plating are recorded by movement of the pointer of a sensitive (+ 0.5um) dilatometer in contact with the tip of a shaft connected to the top end of the strip. Steel strips thicker than 0.05mm can be used for thick or highly stressed deposits, so that the deflections recorded do not approach the elastic limit of the strip. Thermal expansion of the strip is allowed to occur in hot solutions before plating commences. Tensile and compressive stresses are recorded with equal accuracy. The mechanism is frictionless, and is isolated from the solution and the contaminated atmosphere above it by a rubber membrane. Each strip is used once and may then be discarded or kept for reference. Mean deposit thicknesses and current efficiencies are calculated from the weight gain of the strip. It is assumed that the rate of growth of the deposit is constant during plating.

4.0 EXPERIMENTAL DETAILS

4.1 PREPARATION OF SUBSTRATES

Table 2 indicates the steps which were used in preparing the samples before and after the platings.

4.2 PREPARATION OF WATTS PLATING SOLUTION

The nickel solution was made up from individual chemical and brighteners and the following procedure was carried out:

(i) The temperature of the distilled water was raised to approximately 60°C(140°F) and the standard recommended required weights of nickel sulphate mentioned in section(2.0), nickel or sodium choride, boric acid slowly

added to the five litres of distilled water to give the composition given in table 3. This composition was used because for the reason noted in section(2.0). Then the mixture was agitated and well stirred until all the salts have dissolved. (ii)Two and half grammes of activated charcoal powder was added to the made up solution, which was then heated up to 60° , stirred for an hour(using a magnetic stirred-hot plate)and filtered through 542 grade filter paper. This procedure is a standard technique and is used to removed unwanted organic contaminants from the solution by adsorption on to the charcoal particles. Fine filtration then remove the charcoal and any other foreign particles which could otherwise affect the residual stress produced in some deposits.

The pH of the solution was measured at 60°C , (the bath operating temperature), and adjusted to around $\text{pH}=3.75$ using sulphuric acid to decrease the pH, and basic nickel carbonate, $(\text{Ni CO}_3(\text{OH})_2)$, or sodium hydroxide, to increase the pH. All operating conditions are taken from the literature.

4.3 NICKEL-IRON SOLUTIONS

These solutions were made on the basis of Watts solution and their compositions are given in table 3. The procedure of preparing these solutions was exactly the same as Watts solution with the exception of the addition of ferrous sulphate to each individual solution at the end of purification process.

Making of Ni/Fe solutions was on the basis of standard Watts solution and four Ni/Fe solutions with four differ-

ent concentrations of iron were;

1. solution with 0.2 mole per dm^3 of Fe

<u>g/dm³</u>		<u>MASS OF Ni</u>	<u>MASS OF Fe</u>
187.3	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	41.8 g/dm ³	
50	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	12.4 g/dm ³	
55.5	$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$		11.17g/dm ³
30	H_3BO_3		

2. solution with 0.1 mole per dm^3 of Fe

<u>g/dm³</u>		<u>MASS OF Ni</u>	<u>MASS OF Fe</u>
213.6	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	47.7g/dm ³	
50	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	12.4 g/dm ³	
27.7	$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$		5.6g/dm ³
30	H_3BO_3		

3. solution with 0.05 mole per dm^3 of Fe

<u>g/dm³</u>		<u>MASS OF Ni</u>	<u>MASS OF Fe</u>
226.7	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	50.7g/dm ³	
50	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	12.4g/dm ³	
13.9	$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$		2.79g/dm ³

4. solution with 0.025 mole per dm^3 of Fe

<u>g/dm³</u>		<u>MASS OF Ni</u>	<u>MASS OF Fe</u>
233.3	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	52.1g/dm ³	
50	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	12.4g/dm ³	
6.9	$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$		1.4 g/dm ³

Hence ,the above amounts of ferrous sulphate ie, 55.5, 27.7, 13.9 and finally 6.9 were added to the four Ni/Fe solutions in order to replace the Ni in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Using pH range of 3.25-3.5 and operating temperature at 60°C.

4.4 PREPARATION OF COPPER SUBSTRATE AS CATHODES FOR PLATING

Copper was chosen as the cathode substrate material because the nickel deposit and the copper substrate have the same face centred cubic crystal lattice structure(f.c.c), the lattice parameters, (distance between adjacent atomic layers) are similar,ie,

Copper has lattice parameter ' d '= 3.615×10^{-10} m

Nickel has lattice parameter ' d '= 3.524×10^{-10} m

The copper substrates are standard tensile test specimens stamped out of 1mm copper sheet and cut into two to produce two substrates per specimen as shown in fig 12.

The shape and size of this sort of substrate is ideal since a 3.125mm hole could be made in order to suspend it from middle of perspex sheet which covers the solution bath's beaker and having a thin stem is useful for making an electrical connection to the positive side of the current supply.

In order to relieve any internal/surface stresses in the substrate, and to promote an equiaxed grain structure via the processes of recovery and recrystallization, the shot blasted specimen was annealed at 225°C for 20 minutes in an air circulating furnace. After that they were degreased in Trichlorethane using an Ultrasonic bath, and pickled in M/10 sulphuric acid for 20 minutes to remove the thin oxide film produced during annealing. Table 4 shows the steps which were used for Ni or Ni/Fe plating. Substrates were then stored in a desiccator until required for plating in order to keep them dry, clean and thus prevent oxide formation.

4.5 PROGRESSIVE ELECTROLYTIC PURIFICATION OF PLATING SOLUTION VIA 'DUMMYING'

The process of purification was identical in every way for both the Watts and Ni-Fe solutions, so the procedures described below apply to both solutions. Tables 4-5 show the general experimental procedures for Ni or Ni/Fe platings using copper and mild-steel substrates respectively.

4.5.1 'DUMMYING' (125)

The method of purifying the nickel base solution prepared from individual chemicals was carried out to remove the slight traces of metallic and organic contamination which may have been present. The basis of this method was to substitute a large 'dummy' cathode in place of the normal small copper substrates and plate at a low cathode current density for a number of hours. Generally, the accepted value is to 'dummy' a solution for approximately 20 Amp-hours, (the product of cell current and plating time), per litre of solution. This means that for 5.0 litres of solution, a total of $5.0 \times 20 = 100$ Amp-hours dummying will be required. This was done for each solution using the following procedures;

- (a) filtered, undummied solution was heated to 60°C in water bath. The pH was checked and adjusted as necessary to the operating ranges of 3.75-4.0. Two substrates were then plated out, one after the other as described later.
 - (b) a large corrugated copper cathode was placed (cleaned, pickled and degreased), of 400cm^2 into the plating bath.
- Dummying was recommened to be carried out⁽⁷²⁾ at 5mAcm^2

cathode current density. This required a cell current of 2 Amp for the above area of 'dummy' cathode. It has already been stated that dummyming was carried out in $20 \times 5 = 100$ amp-hour stages, so for a cell current at Amps, 50 hours of dummyming per stage was required.

During dummyming, the bath was agitated vigorously by bubbling Argon gas, (inert so that did not react with either electrode), through the plating bath. The bath volume was maintained at 5.0 litres by adding distilled water (shown in fig 13).

(c) two small copper substrates were plated after removing the 'dummy' cathode and adjusting the pH.

(d) the dummyming procedure of (b), was repeated and followed by the plating of (c), until the solution has received a total of 50 amp-hour dummyming.

4.6 USE OF CONVENTIONAL PLATING FOR VARYING CURRENT DENSITIES

OF NI AND Ni-Fe SOLUTIONS

The substrates were plated at bath conditions of constant temperature, 60°C , predetermined pH and the bath concentration for each solution, hence the plating time had to be re-calculated for each current density using the equation given below;

$$W = ItA/ZF$$

Where A=atomic weight of metal deposited

F=Faraday's constant =96,500 coulombs, and is the quantity of electricity required to deposit the equivalent weight in grammes-equivalent weight

t=plating time(seconds)

Z =valency of deposited metal=2 for nickel

I =current in Amps .

To retain the 10 and 25 μ m coating thickness throughout the platings, the range of 20-200mA/cm² current densities were applied to regularly increasing the current density and followed decreasing it . This means that the current density was neither increased nor decreased . This sort of randomization was used to ensure that when the stress in each deposit was determined and plotted in order of regularly increasing cathode current density. Changes therefore followed a regular continuous pattern due solely to the variation in current density .By keeping the variation in current density out of phase with each successive deposit made, such effect would not have the eventual effect of 'swamping' which tends to lose sight of the objectives.

4.7 OPERATION OF PERIODIC PULSE PLATING

A circuit was designed and constructed with the cell unit to produce a periodically pulsed current of varying duration, period, off-time, and current density at the cathode. This circuit and cell are shown in figs 14-15 .

For the varied current density, all the parameters temperature, pH, agitation rate, coating thickness and the duration and period of the pulse were kept constant.

Time of pulse duration on-time of 10mSec 'on' and 'off'-time period of 100mSec. But 'off'-time period was increased from 100 to 200mSec in order to observe the ef-

fects of 'off'-time periods upon stress measurements, composition of Ni/Fe deposits, micro-hardness results and finally the deposit structure.

4.8 PLATING AND USE OF STRESS METER USING THE STRIP MILD STEEL SPECIMENS

These specimens were standard mild steel strips 250mm long * 10mm wide * 0.05mm thick. The length of 15mm at each end of the strip was stopped off with a protective lacquer leaving a length available for plating of 200mm. Internal stress measurements were made using an EFCO internal stress meter. A diagram of the meter is shown on fig 11, and the principle of operation is described by⁽¹²⁶⁾. The meter monitors the expansion or contraction of the mild steel strip whilst metal is being electroplated on to it. After securing the strip in the internal stress meter, the meter was immersed in the electrolyte with the current off. As the temperature of the mild steel strip increased, the strip expanded shown an increase on the dial gauge. Only when the dial gauge reading remained steady, the current switched on. As soon as the current was switched on, the dial gauge readings were noted at one minute intervals for 30 minutes and for longer duration these intervals could be increased to 5 minutes, then the current was switched off. The internal stress meter was removed from the electrolyte and the nickel plated mild steel strip was carefully removed. The strip was rinsed in order to remove excess electrolyte. The protective laquer was dissolved from each end of the strip with acetone and the strip was given a final rinse in acetone before being

allowed to dry in still air. When the strip was completely dry, it was re-weighed to an accuracy of 0.0001g. The strip was handled with nickel tweezers at all times, taking care not to allow any contact with the fingers or any other objects that may have contaminated it. The internal stress of the nickel plate was then determined using the formula given as shown;

$$\text{STRESS} = (Ed/2lt)A \quad (\text{MN/m}^2)$$

E= Young's modulus for mild steel

$$E = 1.97 \times 10^4 \text{ Kgf/mm}^2 = 19 \text{ MN/m}^2$$

l=length of the plated portion of the strip=15 mm

d=thickness of the substrate strip=0.05 mm

A=strain recorded by dialometer(elongation positive, compressive negative), mm

4.9 MICRO-HARDNESS DETERMINATION

In all cases, micro-hardness measurements were taken on the plated deposits of 25 um thickness using a 25 grammes load with a Vickers diamond indenter micro-hardness machine.

First, the samples were plated with copper-cyanide to produce an excess support to the coating thickness in order to withstand the micro-hardness indentations for the deposits resulted from Ni and Ni/Fe baths. Then, the samples were mounted in bakelite and the surface polished back to the one micron surface finish. A minimum of five micro-hardness indentations were taken on each specimen.

4.9.1 SCANNING ELECTRON MICROSCOPY (S.E.M)

Scanning electron microscopy studies of electro-deposited were carried out on plated samples from Watts and Ni/Fe solutions. Energy dispersive X-ray analysis (EDX) was used to determine the percentage of Fe and Ni present in the alloys to be analysed. Samples were mounted in conductive bakelite, polished to one micron surface finish. Percentage of iron and nickel as well as some copper in the alloys can effectively be analysed with the EDX system.

4.9.2 WET ANALYSIS

For the analysis of the alloy composition Ni-Fe alloy deposits electro-plated on copper substrate (0.1 cm * 1.4 cm) were dissolved in a small amount of 50 vol% Nitric acid solution and then, nickel and iron contents were determined by atomic absorption spectroscopy.

4.9.3 ADHESION DETERMINATION

The method of (tape test) ie adhesion test was carried out with mild steel specimens resulting from the Watts bath using the EFCO stress meter in the first set, of experiments . These tests were carried put on specimens such as; 20-200 mA/cm² current densities using pulse plating and conventional plating in Watts solution. The method of 'tape test' according to British standard BS 5411 was followed that an adhesive cellulose tape with an adhesion value of approximately 8 N per 25 mm width, whose adhesive side is applied to the coating under test, using a fixed - weight roller. Care was taken to exclude all air

bubbles and after an interval of 10 seconds, the tape was removed by applying a steady pulling force to the tape, perpendicular to the surface of the coating. The adhesion of the coating was such that there was no evidence of detachment of the coating.

4.9.4 CURRENT EFFICIENCY DETERMINATION

Below equation gives the theoretical maximum mass of substance which can be discharged by a given current in a given time. Current efficiency refers to the cathode product which in practice is less than theoretically predicated. This parameter is defined as;

$$\text{CURRENT EFFICIENCY} = \frac{\text{ACTUAL MASS DISCHARGED}}{\text{THEORETICAL MASS DISCHARGED}} \times 100\%$$

4.9.5 USING X-RAY DIFFRACTION TO DETERMINE THE STRESS WITHIN DEPOSITS

The x-ray diffraction technique allowed stress to be evaluated from the diffraction angle, 2θ , measured at a number of sample orientation angles, ψ . The orientation is varied by rotating the incident beam relative to the component surface. Statistically, the larger the number of specimen tilt values measured (equally spaced in $\sin^2 \psi$) the greater the accuracy of the stress measurement. The principles and operation of the x-ray diffractometer are discussed later.

The working equation for stress analysis⁽¹²⁷⁾ is;

$$\zeta_{\theta} = K_2(2\theta_n - 2\theta_i) \quad \text{-----}(2)$$

Where ζ_{θ} = residual stress

$2\theta_n$ = observed diffraction angle, (peak position), at $\psi = 0^\circ$

$2\theta_i$ = observed diffraction angle, (peak position), at $\psi = 10^\circ$

and $K_2 = E \cot \theta / 2(1 + \nu) + \sin^2 \psi$ ----- (3)

Where E = Young's or elastic modulus = $207 \times 10^9 \text{ Nm}^{-2}$ for Ni

ν = Poissons ratio = 0.36 for Ni.

5.0 EXPERIMENTAL RESULTS

Parameters which involved in pulse plating and conventional plating can be classified by either variables or constants. The former consists of ; cathode current density, concentration of Ni/Fe electrolytes, plating time, 'off-time' and coating thickness. Whereas; the latter consists of; 'on-time', frequency and etc. The aim is to keep these parameters within the optimum range given in the literature.

The numerical values for above parameters are given in tables 6-8 . Parameters such as; frequency, 'off-time' and 'on-time' are not involved in conventional plating.

The effects of the experimental parameters are represented in the following sections.

Tables 6-8 show the variation of solutions, pH and 'off'-time period respectively.

5.1 EFFECT OF CURRENT DENSITY ON PULSE AND CONVENTIONAL PLATING

5.1.1 PULSE PLATING

(a) SURFACE CHARACTERISTICS

Electro-platings were carried out at current densities varying from 2.0 to 200 mA/cm² (0.2-20 A/dm²) for copper substrates and 7.0 to 200mA/cm² (0.7-20 A/dm²) for mild steel substrates respectively.

The surface characteristics of Watts and the Ni/Fe alloys deposits are summarized in tables 9-10 .

Table 9 , indicates the using mild-steel specimens under optimum conditions given in the literature with effect of higher current density, better surface finished and adhe-

sive deposits are produced compared with low current density. Table 10 , indicates the using copper specimens with effect of higher current density,hence,satisfactory surface-finished are produced.

The nickel deposits (Watts) have well-adhered deposit, bright texture and fined-grained at high current density but dull, thin and coarse at lower current density. According to fig 16 , the five samples at various current densities e.g 20-200 mA/cm² have shown these features. Fig 21 shows that with high current density such as 200-250 mA/cm² adhesion was achieved even at low pH value.

The general views and surface appearances of the electro-deposited nickel and nickel-iron alloy obtained from Watts and Ni/Fe baths are shown in figs 16-18 , using copper substrates and figs 19-20 represent the deposits from Watts and Ni/Fe (2), using mild-steel substrates.

(b)COMPOSITION OF PLATING

Using atomic absorption spectroscopy to analyse the nickel and iron contents, the effects of current density on the nickel and iron contents of Ni-Fe alloy deposits obtained from Ni-Fe baths are shown in tables 11-12 . According to tables above, there are increases in the iron-contents as the current density increases. This is also shown that as the iron content of the bath decreases, there is a corresponding decrease in the iron content. Variation of cell efficiency in the nickel/iron and Watts deposits with effect of current density is shown in fig 22 .

Cathode current efficiencies for Ni and Ni/Fe alloy depositions were found to be high compared with conventional plating.

(c) INTERNAL STRESS AND MECHANICAL MEASUREMENTS

The effect of the current density on the internal stress measurements of Ni-Fe alloy and Watts depositions using stressmeter is shown in fig 23 . Under optimum conditions of temperature and pH given in the literature, high current densities have been proved to be beneficial in case of surface appearances (adhesion) and also produced negligible internal stress values which had resulted from Watts, Ni/Fe (4) and Ni/Fe (3) deposits compared with conventional plating. There is also a larger increase in stress but it became less significant at higher current densities.

The hardness of electro-plated copper substrates (25 μ m thick) under a load of 25 grammes was measured using a conventional micro-Vickers hardness tester and average of five readings were taken from this experimental test. This method was carried out with regard to BS5411; part 6: 1981 and the micro-hardness were measured on the cross section of the coatings. The hardness of the Ni and Ni-Fe deposits obtained from Watts and Ni/Fe baths with effect of current density are shown in fig 24 . By comparison with the hardness of pulse plating, the hardness values are almost unchanged with increasing current density in Watts baths. Whereas, these values are drastically changed with high current density in Ni/Fe baths.

5.1.2 CONVENTIONAL PLATING

(a) SURFACE CHARACTERISTICS

Current densities as mentioned above were applied. The deposits were found to be dull and coarse at lower current density in both mild-steel and copper substrates, and improved slightly with an increase in current density, tables 9-10 and figs 25-29 demonstrate the surface appearances and characteristics of deposits obtained from conventional-plating.

In general, pulse plated samples gave better reflectivity than those produced by conventional-plating.

With increase in current density, the cathode current efficiency (C.C.E) increased, reached a maximum and thereafter tend to remain constant. However, with increase in iron- content in bath, the cathode current efficiency diminished to a small extent. This is shown in fig 22 .

(b) INTERNAL STRESS AND MECHANICAL MEASUREMENTS

The effects of current density on the internal stress of Ni-Fe alloy and Watts deposits are shown in fig 23 . The internal stress of Ni-Fe alloy deposits obtained from Ni/Fe (4) and Watts are almost unaffected with increasing current density, However higher internal stresses resulted with conventional-plating compared with pulse. According to the results shown in fig 24 and table 13 , the current density had no significant affect in the hardness of the Watts and Ni/Fe deposits. These results seem to be in good agreement with the Ni and Fe content of the Watts and Ni/Fe deposits shown in table 12 which

demonstrated not to be effective with applying current density. Nevertheless, low hardness values are obtained compared with pulse plating.

5.2 EFFECT OF CONCENTRATION OF ELECTROLYTE ON TYPES OF PLATING

(a) COMPOSITION OF PLATING

In order to show the effects of electrolyte concentration of the baths upon the types of plating, composition of electrolyte were prepared as shown in table 3 .

Table 3 , represents the original bath composition of the Watts and nickel-iron solutions. With change in the concentration of Ni/Fe electrolytes, a wide variation in the composition of the deposit was observed.

It was found that iron (Fe) content in the deposit was always higher than the iron bath. When the bath is richer in iron for example Ni/Fe (1) electrolyte, the deposits obtained are dull and spong in both cases of pulse and conventional plating shown in figs 17,26 , whereas mirror bright (reflective) and fine grained deposits containing 12-21% iron are obtained from the bath having lower iron concentration such as; Ni/Fe (3) and (4) shown in figs 18,27.

(b) INTERNAL STRESS AND MECHANICAL MEASUREMENTS

The variation of the mean internal stress of the Watts and Ni/Fe alloy deposits are shown in tables 14-15. It can be seen that the internal stress values of the Ni-Fe alloy deposits increased with an increase of Fe content

in Ni-Fe solutions, especially in Ni/Fe (1) and (2) solutions. This is also true for deposits resulting from above solutions using X-ray stress measurements. Fig 30 shows the effect of the iron content on the mean stress of the Ni/Fe deposits.

The nickel content in the deposit increases with increase in the nickel concentration in the bath and this is shown in table 11 . As the nickel content increases in bath; Ni/Fe (3) and (4), the nickel (%)percentage also increases. This is true for both pulse and conventional plating, nevertheless, the percentage of nickel in above solution is relatively high in case of conventional plating compared with pulse.

With increase in nickel content in the bath, the cathode current efficiency (C.C.E) increased. This is shown in fig 22 which represents the cathode current efficiency with effect of current density using the Watts and Ni/Fe solutions, a wide range of solutions resulting from Watts and Ni/Fe baths. The Ni/Fe (4), (3) and Watts baths have maximum range of cathode current efficiencies compared with Ni/Fe (1) and (2) solutions.

Variation of hardness with effects of iron and nickel contents are shown in fig 31 . As iron-content in the bath increased, the micro-hardness values were increased. On the other hand with an increase in nickel-content in the bath, these values were diminished.

The use of pulse-plating in Ni/Fe solutions involves the higher content of Ni in deposition at lower current densi-

ty and lower content of Ni in deoposition at higher current density. This is shown in tables 11-12 and figs 32-33 and demonstrates the relationship between the current density and the effect of concentrations of electrolyte.

5.3 EFFECT OF pH ON TYPES OF PLATING

(a) SUBSTRATES

Table 16 shows the effect of variations of pH values on compositions of deposit as determined using the Scanning Electron Microscope. Bright, lustrous and adherent deposits were obtained between pH 3.8-4.0 and 3.4-3.5 in the case of Watts and Ni/Fe solutions using copper specimens.

Lowering the pH values has the most significant effect on the electrodeposition process. As pH range slightly decreased, the composition, micro-hardness and cathode current efficiency values were substantially changed as given in tables 11-13 and figures 34-36.

The range of pH values in these experiments varied from 3.2 to 3.5 and 2.5 to 2.8 in the case of Watts and the Ni/Fe electrolytes respectively. Figure 37 shows the effects of low pH, current density for 10um thickness on the surface finish. Samples 1,2 & 3 in this figure were subjected to the various current densities with low pH. These deposits peeled off badly and therefore internal stress measurements with these deposits were invalid.

(b) STRESS MEASUREMENTS

The stress measurement results from X-ray diffractometry are shown in fig 38 at a fixed pH. The deposit from Watts solution shows lower stress compared with Ni/Fe solutions and these stresses are compressive but the higher Fe concentration in deposits have higher stress levels. The compressive stresses were larger when conventional plating was used with high current densities at a constant pH.

Variation of micro-hardness of the Watts and Ni/Fe alloy deposits with low pH are shown in figure 35 . These values were found to be slightly increased compared with values from figure 24 .

5.4 INFLUENCE OF DURATION OF ELECTROLYSIS ON TYPES OF PLATING

Electro-plating of nickel on to copper substrates has been performed with the duration shown in tables 6-8 . Table 6-8 show the plating time of pulse and conventional plating using Watts and Ni/Fe solutions for constant 10um and 25um thickness respectively. Table 8 indicates the plating time using above solutions but 25um thickness.

As a result of pulse plating, the deposits from Watts bath obtained during 10-27 min were bright and smooth and Ni/Fe deposits were mirror bright (reflective) and fine grained as shown in figs 16-18 . As the duration of electrolysis increased, when using lower current densities such as $20,80\text{mA/cm}^2$, the deposits became dull, loose and nodular with a tendency to peel-off. This was more pronounced in the case of mild-steel specimens shown in Fig 21 . Figure

21 demonstrates this tendency with effect of low current density represented by samples(1&2). Sample(3) exhibited better surface quality with less plating duration but high current density.

Effects of plating time on internal stresses using mild-steel are shown in fig 40 . The results indicated that the shorter plating time and higher current density was significant in creating the low stresses at thin coating thickness.

5.5 EFFECT OF COATING THICKNESS WITH TYPES OF PLATING AND DIFFERENT SUBSTRATES USED

Tables 14-15 show the effects of variation of plating parameters as the mean coating on the increased stresses.

6.0 DISCUSSION

The results presented in section 5.0 have shown how the use of pulse plating may be controlled to give good, low stress deposits of Ni when the following effects are established.

- (1) Effects of current densities upon deposits.
- (2) Effects of plating conditions upon composition of Ni/Fe alloys.
- (3) Effect of coating thickness with types of plating.
- (4) Effect of On-Time to Off-Time.

6.1 EFFECTS OF CURRENT DENSITIES UPON DEPOSITS

As it can be seen from pulse-plating results, increasing current densities have achieved a number of advantages in electrodeposition ;

- (i) Adhesion of the deposit was maintained using 200mA/cm^2 current density, short pulses caused polarisation which results in the small grain size shown in figs 41-42 . The build-up of the small grains produces the better adhesion.
- (ii) Higher current efficiency than in conventional plating has been obtained from all Ni/Fe solutions prepared but slightly better from Watts solution.
- (iii) Bright and mirror bright deposits were made from Ni/Fe(3) and (4) electrolytes.

An extensive study by Burkhardt⁽¹²⁸⁾ showed a wide variety of current distribution effects found in every day plating practice. Increase in the current density results in the rate of formation of nuclei, which give a fine-grained

and adherent deposit. But increase in current density using conventional-plating caused local impoverishment of metal ions round the cathode electrolysis or hydrogen evolution and, as such, the deposits become either dark or unadherent.

Figure 4 shows a schematic representation of the mechanism of cathodic deposition. It would be appear that, by interrupting the plating process, during the time that the current is off for (100 or 200msec), the solution concentration within the so-called diffusion layer, has time to become replenished and nickel atoms(Ni^{2+}) or 'adatom' at the cathode surface shown in same figure have time to migrate to equilibrium sites of lattice. Before reaching the cathode surface the nickel atoms combines with water molecule to form an 'adion'(particulary hydrated/discharged ions), which are then attracted to the cathode and become incorporated in the cathode lattice as it separates from the water molecule. This process is an important part of the overall transfer process.

Using the normal plating, the higher the current density being used, the less time the 'adions' have to find the most suitable discharge sites which could lead to greater distortion in the growing lattice. In practice this distortion would show up as 'stress' in the deposits. The use of pulse plating associated with higher current densities have shown that a less distored lattice can be formed. This type of pulse process is suggested as a means of obtaining smooth and bright deposits. This is displayed by figs 41-42 , showing photographs of a pulse plated Watts deposits made at higher current density. These figures

show bright deposits and smooth deposits was affected by small grains.

6.2 EFFECTS OF PLATING CONDITIONS UPON COMPOSITION OF Ni/Fe ALLOYS

The ratio of nickel ions in the bath to total iron exercises strongly affects on the composition of the deposition. This ratio is by far the most important factor in the operation of the bath with respect to maintaining a specific alloy plating composition. The four different ratio of Ni:Fe baths followed were; 1/5, 1/10, 1/20, 1/40. These solutions were made on the basis of standard Watts solution and their compositions are given in table 3 . The preparation of these solutions were explained in section 4.3 and having the constant weight of nickel chloride and boric acid in each Ni/Fe solutions, the only variable was nickel sulphate and eventually, the small amount of ferrous sulphate was substituted instead of nickel sulphate in four different Ni/Fe solutions. Hence, the total nickel and iron ions were kept constant in each solution.

(a) COMPOSITION OF PLATING

The electrolyte concentration affected the appearance of the platings according to table 11 and figs 17-18 show that mirror bright(reflective) and fine grained deposits containing 12-21% iron are obtained when the Ni:Fe ratio was 1/20 and 1/40.

From the theoretical point of view, Brenner⁽⁷⁰⁾ suggested that the Ni/Fe alloy is interesting in the field of alloy deposits because it is a system which exhibits the

phenomenon of anomalous codeposition, ie, the less noble metal iron deposits preferentially. This is shown in table 11 and this is more pronounced with increasing current density, e.g. Ni/Fe(1) bath using 200mA/cm^2 current density 58-62 % Fe was obtained. Whereas, with the same bath, using 20mA/cm^2 current density compositions of 20.8-29.5 % Fe resulted. This effect was explained by Dahms and Croll⁽⁷³⁾ that when hydrogen evolution proceeds simultaneously with Ni/Fe deposition, a local increase in pH near the electrode surface will be favoured and ferrous hydroxide will be formed in this region. The adsorbed ferrous hydroxide suppresses the deposition of nickel but permits a high rate of ion discharge, hence the less noble metal iron deposits preferentially.

(b) RESIDUAL STRESSES

Effects of Fe content on the internal stress of each solution in Watts and Ni/Fe baths are shown in tables 14-15. With many of the deviations from the mean value due to variations in the quality of the deposit and levels of adherence. After allowances for these deviations, There are percentage of Fe decreases in the bath solution, the internal stresses obtained are reduced. e.g, Ni/Fe(1) bath using 20mA/cm^2 has initiated the internal stress value of 193MN/m^2 but for Ni/Fe(4) bath with the same current density, the stress value is 137MN/m^2 . However, these values are further diminished with higher current density to 60MN/m^2 and 20MN/m^2 from Ni/Fe(1) and Ni/Fe(4) baths respectively.

Direct comparison with other methods of internal stress measurement using the stressmeter has been shown that mean stresses obtained by a modified Stoney's method⁽¹²⁹⁾ gives an indication of the degree of agreement with the tables 14-15 . According to Stoney's method with the modified Watts, the stresses are within range of 64MN/m^2 - 250MN/m^2 which are within the range of above tables and therefore, it can be concluded that with this method of measurement which combines accuracy and semi-continuous recording with ease of operation and sufficient sensitivity for use with all but the thinnest decorative electrodeposits, the most appropriate results may be obtained. Comparison can be made between pulse and normal plating using the same tables as above which indicate that with normal plating, higher stress values were obtained such as 340MN/m^2 but it was lower at 170MN/m^2 using pulse plating from the Ni/Fe(1) and Ni/Fe(4) baths.

It was also found that the internal stresses generated in the electrodeposition of Ni/Fe alloy were highly tensile in case of pulse-plating but as the thickness of plating was increased(e.g, from 10 μm to 25 μm) the compressive stresses became more pronounced. This is shown in table 21 .

The level of internal stress of the Ni/Fe deposits also can be attributed to the lattice mismatch between deposit and substrate of different metals under conditions of assumed epitaxy,(i.e, the deposit continues the structure of the substrate). The model/mechanism is similar to that proposed by Weil^(98,115) but has to be modified to allow for the relaxation processes associated with pulse, on-

time, off-time. The greater this mismatch or misfit between the lattice parameters of the deposit and substrate, then the greater the associated strain energy. Therefore, the internal stress of the Ni/Fe deposits increased with an increase of the iron content and is associated with;

- (i) decreasing the pH of plating
- (ii) increasing the thickness of plating
- (iii) characterising the lattice mismatch between deposit and substrate.

Apart from using atomic absorption spectroscopy to analyse the nickel and iron contents, the scanning electron microscope(E.D.X) also was utilized in order to confirm the results obtained from atomic absorption. These results are shown in table 16 . The limitation of the E.D.X system on these electroplated samples is the excitation of the substrate such as copper and mild steel which were detected below the plated surface. Therefore, some copper percentage were detected by this method and from these results it can be seen that the atomic absorption spectroscopy method has produced a slightly different results compared with scanning electron microscope. These changes can only be observed with normal plating not pulse-plating. The variation of Ni and Fe content from scanning electron microscope(E.D.X) are similar to these obtained by Nakamura⁽¹³⁰⁾.

(C) CURRENT DENSITY

Table 16 indicates that as high current density was used, the percentage of iron decreases with Ni/Fe(2), Ni/Fe(3) and Ni/Fe(4) electrolytes. The percentage of iron

from 21.3 in Ni/Fe(1) electrolyte decreased to 12.3 in Ni/Fe(4) respectively. This confirms that with higher pH there is more iron in the deposit compared with the conventional.

Tables 11-12 show the composition of Ni and Fe deposits under the conventional plating are slightly different with respect to current density and pH solution in Ni/Fe(1) (under the influence of conventional-plating). However, the result from these tables appeared to be similar to those obtained by Nakamura⁽¹³⁰⁾ for pulse-plating.

The alloy compositions of electrodeposited Ni/Fe dependence upon the parameters of pulsating current are quite contrary to Maksimovie⁽⁴³⁾ statement. This reference indicates that the alloy composition would not be affected by the pulsating current. However, in fig 32 and tables 11-12 show that composition of Ni/Fe alloy is affected by current density, plating time, off-time period.

The composition and properties of electrodeposited Ni/Fe alloys depend upon the composition of the solution from which they are plated and the deposition conditions. Variables which are significant in the deposition process include pH, current density, off-time period, temperature and variation in concentration of all of the solution components.

(d) TYPES OF PLATING

Tables 14-15 show a comparison between pulse and conventional plating used, for various current density. Results indicate that pulse plating deposits for all solutions give lower residual stress values compared with

direct current process.

Dvorak and Vrobel⁽¹³¹⁾ found that with using d.c normal plating , there is a progressive increase in stress as current density of 50mA/m^2 was applied and the stress values are relatively high compared with results from tables(14-15). Nevertheless, they added the addition agents to the Watts solution. This effect was confirmed by Barrett, Diggin, Fanner and Kendrick⁽⁸⁴⁻⁸⁵⁾ who proposed the theory of the crystallite joining theories . Their observations were made as the current density increased, so the residual stresses increased using coventional plating. The reason was due to increased nucleation rate caused by an increase in overpotential, leading to more joining of crystallites.

(e) MICRO-HARDNESS

An effect shown by fig 35 is the consistently higher micro-hardness of the higher Fe percentage in Ni/Fe electrolytes compared with the lower Fe percentage in Ni/Fe electrolytes. Therefore, it is clear from fig 35, which also includes data for Watts deposits, that as iron-content in the bath increased, the micro-hardness values were increased but on the other hand with an increase in nickel-content in the bath, these values were diminished. Therefore, it can be concluded that an increase in the micro-hardness of the Ni/Fe alloy deposits seemed to be attributable to an increase in Fe-content in Ni/Fe electrolyte.

The pulse plating has shown by fig 32 and table 11 that

the higher content of Ni occurs when plating at lower current density and lower content of Ni when using higher current density , vice versa with the Fe-content. These results seem to be in good agreement with theory of Brenner⁽⁷⁰⁾ that the less noble metal iron metal iron deposits preferentially compared with noble metal nickel.

6.3 EFFECTS OF COATING THICKNESS WITH TYPES OF PLATING

There are two major factors would influence the deposit thickness. First, there is the immediate influence of the basis metal surface in the initial crystal structure because , if there is to be a true atomic bond, the depositing metal must by some means combine its lattice to that of the basis metal. Second, there is the nature and content of the cathode film. These two factors mentioned above are related to the metal deposit when it is being formed and must be the controlling factors.

(a)EFFECTS OF COATINGS UPON INTERNAL STRESSES

Tables 14-15 show the variation of mean coating thickness on the increased stresses. High tensile instantaneous stresses have always been found in the initial stage of deposition. This initial stress was not substantially influenced in any general way by temperature or cathode current density. It appears to be due to the influence of the basis metal structure on the different lattice of the deposit, an influence that persists to some degree to considerable thickness. It may well be characteristic of a deposit having preferred orientation partly determined by

the early nickel layers.

Tensile stresses can be considered to be due to deposits being dimensionally less than the previously laid down one. As crystal defects such as dislocation occupy a layer specific volume than a perfect lattice, a decrease in the dislocation density with thickness could cause tensile stresses to be developed during the deposition in the range of (1-3.5)um thickness as shown in table 14 . From these results, it can be seen that increasing coating thickness would create compressive stresses under optimum conditions.

6.4 EFFECT OF ON-TIME TO OFF-TIME

Pulsed- current electrolysis with ratio of on-time to off-time of 10/100 and 10/200msec have been applied to the deposits of Watts and Ni/Fe solutions. In pulse-plating, the off duty factor, the pulse duration and the current density are all related to obtaining a high quality plating rate at least comparable to normal plating. The surface morphology of nickel deposits plate with pulsating current of periods in the 10msec on and 100msec off range and with fixed average plating current density of $250\text{mA}/\text{cm}^2$ are affected significantly. This significant factor was observed during the pulse plating process and this is shown in figs 41-42. Figure 42 shows that at given amplitude and pulse length, an increase of the off-time led to decrease in the grain size of nickel deposits. The pulse amplitude or current density was $250\text{mA}/\text{cm}^2$ and pulses time was 10msec, using the off-time produced finer/small grains. The most plausible explanation is the

adsorption of an inhibiting species which block the growth centres of the cathode during the off-time, this forces the system to create new nuclei at each new pulse. Therefore, the longer the off-time, the finer the grains. The inhibitors probably were the sulphate anions and thus, for nickel deposition, an increase in off-time was accompanied by decrease in grain size.

These results are in good agreement with Puippe and Ibl⁽²⁾. They explained these features are due to the availability of high current density in pulse-plating which generates free energy and because the free energy for the electrode reaction is much higher than that for direct current. Therefore, this influence strongly the crystallization features, As the nucleation rate is enhanced due to the crystallization, the final grain size become smaller.

Figure 24 and table 13 show the variation of micro-hardness values of Watts and Ni/Fe deposits with off-time period. The micro-hardness values decreased as longer off-time period was used. As a result of increasing off-time period, the iron content in deposits decreases as shown in tables 18-19. Also figure 39 and table 13 show the variation of iron, nickel contents, solution pH (high and low) and finally longer off-time. The values of hardness decreased further more due to diminishing the iron-content in the deposit with longer off-time period.

Summary of pulse plating features are shown in fig 43 as an aid to the ofequipment. The use of pulse generator,

copper coulometer, oscilloscope, power mosfets distinguishes the pulse plating procedure from conventional plating arrangements. This gives an additional means of controlling the quality of deposits in terms of properties, grain size, thickness, stress level and surface roughness as shown in the figure 43.

7.0 CONCLUSIONS

A study was undertaken to define the processing parameters which control the characteristics of the electro-deposits behaviour in pulse plating. The control of electrodeposition by means of pulse plating has been investigated and the following conclusions drawn:

- (1) The composition of Ni/Fe deposits have been affected mainly by the electrolyte concentration, current density and to some extent by solution pH.
- (2) Adhesion was observed with higher current density and the use of higher current densities has been proved to be beneficial in obtaining the adhesive deposits on substrates.
- (3) Bright and reflective deposits were produced from Ni/Fe solutions.
- (4) The use of Ni/Fe electrolytes with lower iron content have been demonstrated and these electrolytes are the most suitable for producing better quality deposits.
- (5) Higher cathode current efficiencies have been achieved with higher current densities using pulse plating.
- (6) The smaller grain size was observed from higher current densities using the Watts solution with aid of pulse plating.
- (7) The reduction in Ni:Fe ion ratio in Ni/Fe solution resulted in reduction of nickel content of the Ni/Fe deposits.
- (8) Low current densities caused higher tensile stress in pulse plating with respect to thin coating thickness but not in as great a degree as does thick coating.
- (9) Micro-hardness data showed a distinct difference

between DC and pulsing due to the processing technique. The pulse plated alloys were consistently harder than the direct plated alloys, with the highest hardness number at the highest current density used.

(10) The metals electrodeposited by pulse plating have a reduced internal stress compared with the coatings of the same thickness deposited by conventional plating.

(11) In normal-plating, greater deposition or 'burning'/peeling occurred in the high current density areas of the workpiece. This effect is greatly reduced and improved deposit distribution by means of a pulse current.

(12) The current efficiencies of Watts and prepared Ni/Fe solutions were compared and it demonstrated that the Watts solution has the higher current efficiency.

8.0 SUGGESTIONS FOR FURTHER WORK

Further work should be carried out to investigate the off-time and on-time periods. It was concluded that the off-time must be the most important factor and this could affect the surface morphology during the off period. This is why this parameter should be investigated with longer off-time compared with the previous one (100-200mSec). The range of 200-400mSec off-times associated with optimum value for on-time would influence the current efficiency as well as the deposit surface. Where the solution employed contains more than one species of metal ion then it may be possible, using a combination of high current density and longer off time period, to discharge all metal ions present in the boundary layer adjacent to electrode surface before the onset of concentration polarisation. Such a mode of deposition might be expected to produce coherent alloy deposits rather than the powdery deposits usually formed during conventional D.C discharge involving concentration polarization.

Looking back at the data and photographs of surface morphology results from copper substrates are the most reliable and consistent and therefore these data demonstrate that there is a clear opportunity to allow more precise interpretation of processing parameter using copper strip rather than mild-steel strips, even though sensible coatings were produced from mild-steel. These two techniques can be compared to show effects of using different substrates.

The next step would involve the use of additive such as, Saccharine on Ni and Ni/Fe solutions. Addition of Saccharine or stabilizing agents will stabilize the formation of ferric ions in bath resulting from oxidation of the ferrous salts. As iron concentration in all bath solutions is the most important factor in deposition e.g, composition rate, stress level, thickness of plating and also determining the mechanical properties. The effects of Fe content on the internal stress are significant and it was found that with lowering Fe content in deposits, would create the lower stress and using additives would further decrease the internal stress levels. Also the development of mathematical model for the action of the periodically changing current which produces the specified composition is proposed.

The further stage of future work would involve the varying temperature of plating of the bath with an optimum current density under the optimum range of periods, exploring effect of temperature change on the nature of deposits. The stresses could be lowered with varying bath temperature at low current densities. This is possibly due to higher diffusion rates giving rise to less unfilled space between crystallites upon coalescence but this could encourage the formation of ferric ions in Ni/Fe solutions.

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Table.1

LIST OF COMPONENT USED FOR PULSE-PLATING(P.P)&CONVENTION
PLATING (C.P)

1. power Mosfets.
2. Double beam oscilloscope.
3. Power supply.
4. Pulse generator.
5. Copper coulometer.
6. The EFCO (dilatometer).
7. The stirrer (using Argon-gas).
8. Pump-generator,
9. pH-meter.

TABLE.2

STEPS WHICH WERE USED FOR NICKEL OR NICKEL-IRON PLATING
WITH FRESH SOLUTION FORMULATIONS

1. Visual inspection for either copper or mild-steel specimens.
2. Shot blasting (for copper specimens).
3. Cleaning the sample.
4. Cathodic clean(five minutes per sample).
5. Wash the sample before the plating.
6. Weight the sample before and after plating.
7. Nickel or nickel-iron plating + copper coulometer solution.
8. Wash the sample after the plating.
9. Cold soaks, (mild-steel specimens must be soaked in acetone in order to remove the lacomit).
10. Dry the sample.
11. Keep the sample in desicator.

TABLE.3BATH COMPOSITION OF THE WATTS AND NICKEL-IRON ELECTROLYTES

TYPE	NICKEL SULPHATE	NICKEL CHLORIDE	BORIC ACID	IRON SULPHATE	CITRIC ACID
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ g/l	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ g/l	H_3BO_3 g/l	$\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ g/l	g/l
WATTS	240	50	30	--	--
Ni/Fe(1)	187.33	50	30	55.5	0.6
Ni/Fe(2)	213.6	50	30	27.75	0.6
Ni/Fe(3)	226.7	50	30	13.88	0.6
Ni/Fe(4)	233.3	50	30	6.94	0.6

Table.4

STEPS WHICH WERE INVOLVED IN Ni OR Ni/Fe PLATING (FOR
COPPER SUBSTRATES)

PRE-PLATING INSPECTION

- | | |
|---------------------------------|---------------------------------------|
| (1) HEAT-TREATMENT | annealed at 225^0 for 20
minutes |
| | (a) Dummying |
| (2) PURIFICATION | (b) Filtration/Decontamination |
| (3) CLEANING | (a) solvent degreasing |
| | (b) soak cleaning |
| | (c) Ultrasonic cleaning |
| | (d) Electrolyte cleaning |
| (4) PREPARATION OF
SUBSTRATE | (a) Lacomit cover |
| | (b) wait for lacomit to dry |
| | (c) Etch with 20% H_2SO_4 |
| (5) Ni or Ni/Fe PLATING | (a) Pulse-plating |
| | (b) Convention-plating |
| (6) POST-PLATE TREATMENTS | (a) Acid dip |
| | (b) Anti-tarnish treatment |
| | (c) Laquer |
| (7) DRYING | (a) Use of adsorbant |
| | (b) Use of hot air |
| | (c) vapour drying |

TABLE.5

STEPS WHICH WERE INVOLVED IN NI OR NI/FE PLATING (FOR
MILD-STEEL SUBSTRATES)

PRE-PLATING INSPECTION

- | | |
|---------------------------------|--|
| (1) PURIFICATION | (a) Dummying |
| | (b) Filtration/
decontamination |
| (2) CLEANING | (a) Solvent degreasing |
| | (b) Soak cleaning |
| | (c) Ultrasonic cleaning |
| | (d) Electrolyte cleaning |
| (3) PREPARATION OF
SUBSTRATE | (a) Lacomit cover |
| | (b) Wait for lacomit to dry |
| | (c) Etch with 20% H ₂ So ₄ |
| (4) NI OR NI/FE PLATING | (a) Pulse-plating |
| | (b) Conventional-plating |
| (5) POST-PLATE TREATMENTS | (a) Acid dip |
| | (b) Anti-tarnish treatment |
| | (c) Laquer |
| (6) Drying | (a) Use of adsorbant |
| | (b) Use of hot air |
| | (c) Vapour drying |

TABLE.6

THE PARAMETERS WHICH INVOLVED IN BOTH PULSE PLATING(P.P)
AND CONVENTIONAL PLATING(C.P), USING WATTS SOLUTION.
THE FOLLOWING PARAMETERS PARAMETERS KEPT CONSTANT;

- (*) FREQUENCY=9.1HZ
- (*) OFF-TIME=100msec
- (*) ON-TIME=10msec
- (*)TEMPERATURE=60C
- (*) pH =3.75-4.0

CURRENT DENSITY (mAcm ⁻²) (#)	THICKNESS (um) (#)	PLATING-TIME (min) (#)
---	--------------------------	------------------------------

(PULSE-PLATING)

20	10	277.4
40	10	139.0
80	10	69.4
120	10	46.2
160	10	34.7
200	10	27.7

(CONVENTIONAL-PLATING)

20	10	25.2
40	10	12.6
80	10	6.3
120	10	4.2
160	10	3.1
200	10	2.5

(PULSE-PLATING)

20	25	694
80	25	173
200	25	69

(CONVENTIONAL-PLATING)

20	25	63
80	25	15.5
200	25	6.5

(#), indicates variable
(*), indicates constant

TABLE.7

THE PARAMETERS WHICH INVOLVED IN BOTH PULSE PLATING(P.P)
AND CONVENTIONAL PLATING(C.P), USING Ni/Fe SOLUTION.

THE FOLLOWING PARAMETERS PARAMETERS KEPT CONSTANT;

- (*) FREQUENCY=9.1HZ
- (*) OFF-TIME=100msec
- (*) ON-TIME=10msec
- (*)TEMPERATURE=60C
- (*) pH =3.35-3.50

CURRENT DENSITY (mAcm ⁻²) (#)	THICKNESS (um) (#)	PLATING-TIME (min) (#)
---	--------------------------	------------------------------

(PULSE-PLATING)

20	10	277.4
40	10	139.0
80	10	69.4
120	10	46.2
160	10	34.7
200	10	27.7

(CONVENTIONAL-PLATING)

20	10	25.2
40	10	12.6
80	10	6.3
120	10	4.2
160	10	3.1
200	10	2.5

(PULSE-PLATING)

20	25	694
80	25	173
200	25	69

(CONVENTIONAL-PLATING)

20	25	63
80	25	15.5
200	25	6.5

(#), indicates variable

(*), indicates constant

TABLE.8

THE PARAMETERS WHICH INVOLVED IN BOTH PULSE PLATING(P.P)
AND CONVENTIONAL PLATING(C.P).

THE FOLLOWING PARAMETERS KEPT CONSTANT;

- (*) FREQUENCY=4.8HZ
- (*) OFF-TIME=200msec
- (*) ON-TIME=10msec
- (*)TEMPERATURE=60C
- (*) THICKNESS=25um

CURRENT DENSITY (mAcm ⁻²) (#)	pH (#)	PLATING-TIME (min) (#)
---	-----------	------------------------------

(PULSE-PLATING) USING Ni/Fe SOLUTIONS

20	3.35-3.50	529.6
80	3.35-3.50	131.7
200	3.35-3.50	51.5

(PULSE-PLATING) USING WATTS SOLUTIONS

20	3.75-4.0	529.6
80	3.75-4.0	131.7
200	3.75-4.0	51.5

(PULSE-PLATING) USING Ni/Fe SOLUTIONS

20	2.5-2.8	529.6
80	2.5-2.8	131.7
200	2.5-2.8	51.5

(PULSE-PLATING) USING WATTS SOLUTIONS

20	3.2-3.5	529.6
80	3.2-3.5	131.7
200	3.2-3.5	51.5

(#), indicates variable
(*), indicates constant

TABLE.9

CHARACTERISTICS AND SURFACE APPEARANCES OF Ni AND Ni/Fe ALLOYS DEPOSITS USING 'MILD-STEEL' SPECIMENS WITH EFFECTS OF CURRENT DENSITY, SOLUTION pH, TYPES OF PLATING AND PREPARATION OF SUBSTRATES RESULTING FROM WATTS AND Ni/Fe SOLUTIONS.

SOLUTIONS	WATTS	Ni/Fe(1)	Ni/Fe(2)	Ni/Fe(3)	Ni/Fe(4)
PULSE-PLATING					
HIGH CURRENT DENSITY	well-adhered & bright	dark & semi-bright	reflective around edges	reflective	reflective & lustrous
LOW CURRENT DENSITY	dull	dark	dull	semi-bright	bright
LOW pH	peeled-off	peeled-off badly	peeled-off badly	peeled-off badly	peeled-off badly
CONVENTIONAL-PLATING					
HIGH CURRENT DENSITY	dull	dark & coarse	dark & coarse	dull	bright but not reflective
LOW CURRENT DENSITY	dull	dark & coarse	dark	dark	dull
LOW pH	peeled-off	peeled-off badly	peeled-off badly	peeled-off badly	peeled-off badly

TABLE.10

CHARACTERISTICS AND SURFACE APPEARANCES OF Ni AND Ni/Fe ALLOYS DEPOSITS USING 'COPPER' SPECIMENS WITH EFFECTS OF CURRENT DENSITY, SOLUTION pH, TYPES OF PLATING AND PREPARATION OF SUBSTRATES RESULTING FROM WATTS AND Ni/Fe SOLUTIONS.

SOLUTIONS	WATTS	Ni/Fe(1)	Ni/Fe(2)	Ni/Fe(3)	Ni/Fe(4)
PULSE-PLATING					
HIGH CURRENT DENSITY	well- adhered& bright	dull	reflective	reflective	reflective
LOW CURRENT DENSITY	semi- bright	dull & dark	dull	semi-bright	bright
LOW pH	dull & coarse	dark &semi- adhered	dark	dull	semi-bright
CONVENTIONAL-PLATING					
HIGH CURRENT DENSITY	dull	dull	dark	semi-bright	bright but not reflective
LOW CURRENT DENSITY	dull & coarse	dark ,dull& coarse	dark	dark	bright
LOW pH	dark	semi- adhered	dark	dark	semi-bright

TABLE 11

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, TYPES OF PLATING AND 'OFF'-TIME PERIOD UPON THE Ni/Fe DEPOSITS USING ATOMIC ABSORPTION TO DETERMINE THE NICKEL(Ni)% AND IRON(Fe)%.
 COATING THICKNESS=10um
 USING 10 msec 'ON'
 100 msec 'OFF'

CURRENT DENSITY mAcm ⁻²	HIGH pH=3.35-3.50		LOW pH=2.50-2.80	
	IRON Fe%	NICKEL Ni%	IRON Fe%	NICKEL Ni%
		Ni/Fe(1) SOLUTION		
20(P.P)	20.8 \pm 3.1	79.2 \pm 2.5	29.5 \pm 2.1	70.5 \pm 1.7
20(C.P)	44.5 \pm 2.2	55.5 \pm 4.9	52.1 \pm 2.7	47.9 \pm 2.9
80(P.P)	53.2 \pm 1.1	46.8 \pm 3.8	59.2 \pm 1.5	40.8 \pm 5.5
80(C.P)	39.0 \pm 3.4	60.9 \pm 4.5	48 \pm 2.9	52 \pm 4.9
200(P.P)	58.1 \pm 2.5	41.9 \pm 2.5	62.2 \pm 6.5	37.8 \pm 4.7
200(C.P)	36.0 \pm 3.7	63.9 \pm 3.5	47.7 \pm 5.2	52.3 \pm 3.5
		Ni/Fe(2) SOLUTION		
20(P.P)	15.7 \pm 2.5	84.3 \pm 4.5	24.5 \pm 3.3	75.5 \pm 4.5
20(C.P)	37.3 \pm 3.5	63.7 \pm 5.6	42.5 \pm 2	57.5 \pm 4.3
80(P.P)	35.9 \pm 5.6	64.0 \pm 2.1	38.1 \pm 1.7	61.9 \pm 2.5
80(C.P)	27.1 \pm 6.1	72.8 \pm 3.1	34.5 \pm 2.5	65.5 \pm 4.4
200(P.P)	38.6 \pm 5.6	61.4 \pm 4.2	43.5 \pm 6.1	56.5 \pm 4.7
200(C.P)	19.0 \pm 5.5	80.9 \pm 3.2	33.5 \pm 3.5	66.5 \pm 5.2
		Ni/Fe(3) SOLUTION		
20(P.P)	21.1 \pm 9	78.9 \pm 2.0	29.5 \pm 3.9	70.5 \pm 2.2
20(C.P)	27.7 \pm 4.1	72.3 \pm 3.1	33.1 \pm 3.7	66.9 \pm 1.7
80(P.P)	26.8 \pm 2.5	73.2 \pm 5.6	30.5 \pm 4.6	69.5 \pm 2.1
80(C.P)	24.8 \pm 1.7	75.2 \pm 4.8	27.5 \pm 4.7	72.5 \pm 3.1
200(P.P)	25.8 \pm 2.8	74.2 \pm 3.7	29.7 \pm 5	70.2 \pm 4.6
200(C.P)	8.2 \pm 3.6	91.8 \pm 4.9	25.5 \pm 5.0	74.5 \pm 4.6
		Ni/Fe(4) SOLUTION		
20(P.P)	12.4 \pm 2.1	87.6 \pm 2.5	20.5 \pm 4.1	79.4 \pm 3.5
20(C.P)	13.7 \pm 3.5	86.3 \pm 3.5	21.2 \pm 2.5	78.8 \pm 3.3
80(P.P)	14.5 \pm 1.7	85.5 \pm 4.1	17.5 \pm 1.9	82.5 \pm 3.9
80(C.P)	4.8 \pm 1.9	95.2 \pm 3.8	19.5 \pm 2.6	80.5 \pm 4.5
200(P.P)	17 \pm 2.9	83 \pm 2.5	23.5 \pm 5.2	76.5 \pm 4.1
200(C.P)	2.5 \pm 4.1	97.5 \pm 3.2	6.5 \pm 5.1	93.5 \pm 2.9

(P.P), indicates pulse-plating.

(C.P), indicates conventional-plating.

TABLE.12

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, TYPES OF PLATING AND 'OFF'-TIME PERIOD WERE UPON THE Ni/Fe DEPOSITS USING ATOMIC ABSORPTION TO DETERMINE THE NICKEL(Ni)% AND IRON(Fe)%.

COATING THICKNESS=25um
USING 10 msec 'ON'
100 msec 'OFF'

CURRENT DENSITY mAcm ⁻²	HIGH pH=3.35 TO 3.5		LOW pH=2.50 TO 2.8	
	IRON Fe%	NICKEL Ni%	IRON Fe%	NICKEL Ni%
Ni/Fe(1) SOLUTION				
20(P.P)	20±1.1	82±5.2	39±3.9	61±1.8
20(C.P)	29.6±.7	70.4±4.4	38.3±5.2	61.7±4.4
80(P.P)	25.3±4.2	74.7±5.9	47.1±3.3	52.9±5.5
80(C.P)	32.5±2.1	67.5±4.5	42.2±1.2	57.8±5.2
200(P.P)	30±3.1	70±3	35.7±1.2	64.3±5.3
200(C.P)	28.8±3.1	71.2±3.7	39.0±1.9	60.9±4.3
Ni/Fe(2) SOLUTION				
20(P.P)	13.5±5.7	86.5±3.7	29.5±1.1	70.5±5.1
20(C.P)	23.8±4.5	76.2±5.1	29.5±4.9	70.5±5.6
80(P.P)	23.0±3.7	76.9±4.2	37.5±4.6	62.5±4.9
80(C.P)	21.1±5.1	78.8±3.6	24.5±4.5	75.5±3.7
200(P.P)	23.6±4.7	76.3±3.7	29.5±4.5	70.5±2.1
200(C.P)	14.5±2.2	85.4±2.8	27.5±1.23	72.5±4.9
Ni/Fe(3) SOLUTION				
20(P.P)	13.2±4.4	86.7±2.9	17.5±3.4	82.5±3.3
20(C.P)	20.7±6.5	79.3±5.8	20±3.2	80±4.5
80(P.P)	12.7±4.3	87.3±7.8	23.5±1.4	76.5±2.2
80(C.P)	21.7±6.3	78.3±7.9	27.7±1.7	72.3±.75
200(P.P)	18.9±1.8	81.1±6.9	19.1±3.3	80.9±1.6
200(C.P)	15.3±5.5	84.6±3.1	27.5±4.5	72.5±2.9
Ni/Fe(4) SOLUTION				
20(P.P)	10±5.3	90±3.3	15±2.2	85±3.9
20(C.P)	14.4±3.2	85.6±4.5	22.5±6.5	77.5±3.9
80(P.P)	13.9±6.1	86.1±3.5	17.5±3.5	82.5±3.4
80(C.P)	7.8±3.4	92.2±4.8	12.5±4.1	87.5±4.6
200(P.P)	12.0±.8	87.9±3.2	21.1±2.56	78.89±2.
200(C.P)	4.5±2.6	95.5±2.6	10.5±3.4	89.5±.25

(P.P), indicates pulse-plating.

(C.P), indicates conventional- plating.

TABLE 13

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, TYPES OF PLATING (ONLY PULSE-PLATING WAS APPLIED) AND LONGER 'OFF'-TIME PERIOD UPON VARIATION OF MICRO-HARDNESS OF ELECTRO-DEPOSITED(COPPER) SPECIMENS FROM THE NICKEL-IRON AALLOY AND WATTS DEPOSITS.

COATING THICKNESS=25um
USING 10 msec 'ON'
200 msec 'OFF'

solutions	CURRENT DENSITY mAcm ⁻²	HIGH pH	MEAN Hv	LOW pH	MEAN Hv
WATTS (P.P)	20	3.9	285 \pm 3.1	3.4	288 \pm 8.8
	80	4	267 \pm .5	3.2	278 \pm 7.5
	200	3.9	288 \pm 11.1	3.1	295 \pm 10.1
Ni/Fe(1) (P.P)	20	3.4	365 \pm 12.2	2.8	375 \pm 13.5
	80	3.5	399 \pm 21.1	2.7	388 \pm 12.5
	200	3.3	390 \pm 16.2	2.8	411 \pm 35
Ni/Fe(2) (P.P)	20	3.5	343 \pm 13.1	2.8	353 \pm 10.5
	80	3.3	355 \pm 17.7	2.8	377 \pm 6.7
	200	3.4	395 \pm 18.8	2.8	421 \pm 39.9
Ni/Fe(3) (P.P)	20	3.3	298 \pm 25	2.8	288 \pm 19.5
	80	3.35	340 \pm 17.5	2.7	359 \pm 21.5
	200	3.5	352 \pm 5.5	2.6	372 \pm 34.5
Ni/Fe(4) (P.P)	20	3.5	296 \pm 12.7	2.5	251 \pm 2.2
	80	3.4	342 \pm 13.5	2.6	346 \pm 3.5
	200	3.5	302 \pm 8.5	2.8	312 \pm 14.9

(P.P), indicates pulse-plating.

TABLE 14

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, PLATING TIME, MEAN COATING THICKNESS, TYPES OF PLATING AND FINALLY 'OFF'-TIME PERIOD UPON THE NICKEL-IRON ALLOY AND WATTS DEPOSITS USING STRESSMETER TO DETERMINE THE MEAN STRESS IN THE ABOVE DEPOSITS.

COATING THICKNESS=3.5um

USING, 10msec 'ON'-TIME

100msec 'OFF'-TIME

Solution	CURRENT DENSITY mAcm ⁻²	Plating time (Min)	Average thickness (Um)	Mean average value of stress MNm ⁻² *10
		pH=3.75 TO 4.0		
WATTS	7	277	2.3	11±2.1
(P.P)	28	69	1.6	5.7±5.5
	70	27	2.3	4.7±1.6
WATTS	7	25.1	2.3	4.3±.9
(C.P)	28	6.3	2.3	13.5±2.1
	70	2.4	2.2	10.5±1.2
		pH=3.35 TO 3.50		
Ni/Fe(1)	7	277	2.3	21.3±7.1
(P.P)	28	69	1.6	8.0±5.3
	70	27	2.3	8.3±4.3
Ni/Fe(1)	7	25.1	2.3	1.2±.4
(C.P)	28	6.3	1.5	23±7.1
	70	2.4	2.2	27.5±9.5
		pH=3.35 TO 3.50		
Ni/Fe(2)	7	277	2.5	18.5±3.1
(P.P)	28	69	1.8	10.2±5.2
	70	27	2.4	7.1±4.4
Ni/Fe(2)	7	25.1	2.1	3.1±3.1
(C.P)	28	6.3	1.8	19.5±6.2
	70	2.4	2.3	19±11.1
		pH=3.35 TO 3.50		
Ni/Fe(3)	7	277	2.3	16.5±2.3
(P.P)	28	69	1.9	11.2±8.5
	70	27	1.9	4.8±1.0
Ni/Fe(3)	7	25.1	2.2	4.1±1.9
(C.P)	28	6.3	2	17.9±2.2
	70	2.4	1.9	16±5.6
		pH=3.35 TO 3.50		
Ni/Fe(4)	7	277	2.1	14.3±12.2
(P.P)	28	69	1.2	20.7±10.5
	70	27	1.6	3.9±.7
Ni/Fe(4)	7	25.1	2.2	5.1±2.0
(C.P)	28	6.3	1.2	15.5±3.9
	70	2.4	1.2	12.2±9.3

(P.P), indicates pulse-plating.

(C.P), indicates conventional-plating.

TABLE 15

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, TYPES OF PLATING, MEAN COATING THICKNESS, PLATING TIME AND FINALLY 'OFF'-TIME PERIOD UPON THE Ni/Fe ALLOY AND WATTS DEPOSITS USING STRESSMETER.

USING, 10 msec 'ON'-TIME

100 msec 'OFF'-TIME

SOLUTIONS	CURRENT DENSITY mAcm ⁻²	PLATING TIME (Min)	AVERAGE THICKNESS (μ m)	MEAN AVERAGE VALUE OF STRESS MNm ⁻² *10
pH=3.75 TO 4.00				
WATTS (P.P)	20	277	5.2	4.1 \pm 2.8
	40	137	5	10.0 \pm 8.5
	80	69	7.125	6.2 \pm 4.2
	120	46	7	3.0 \pm 2.2
	160	34	7.25	.4 \pm .3
	200	27	8.33	.3 \pm .4
WATTS (C.P)	20	25.1	6.03	18.5 \pm 10.0
	40	12.4	7.01	21.5 \pm 3.4
	80	6.3	7.25	17.7 \pm 3.3
	120	4.1	7.125	9.1 \pm 3.4
	160	3.0	6.69	15.9 \pm 3.3
	200	2.4	8.25	11.1 \pm 2.2
pH=3.35 TO 3.50				
Ni/Fe(1) (P.P)	20	277	6.3	19.3 \pm 3.1
	40	137	7.8	17.6 \pm 5.5
	80	69	8.4	8.0 \pm 1.2
	120	46	6.9	8.1 \pm .9
	160	34	5.9	7.3 \pm 2.2
	200	27	7.8	6.3 \pm 3.2
Ni/Fe(1) (C.P)	20	25.1	7.3	34.4 \pm 2.1
	40	12.4	7.4	32.5 \pm 4.3
	80	6.3	7.1	29.0 \pm 2.9
	120	4.1	7.2	16.6 \pm 3.3
	160	3.0	6.3	15.5 \pm 1.1
	200	2.4	5.3	12.2 \pm 2.9

(P.P), indicates pulse-plating.

(C.P), indicates conventional-plating.

CONTINUATON OF TABLE 15

SOLUTIONS	CURRENT DENSITY mAcm ⁻²	PLATING TIME (Min)	AVERAGE THICKNESS (um)	MEAN AVERAGE VALUE OF STRESS MNm ⁻² *10
pH=3.35 TO 3.50				
Ni/Fe(2) (P.P)	20	277	5.9	19.1±1.7
	40	137	7.3	17.2±5.5
	80	69	6.6	9.5±1.1
	120	46	7.3	8.7±2.2
	160	34	6.4	6.3±3.6
	200	27	8.2	6.0±2.1
pH=3.35 TO 3.50				
Ni/Fe(2) (C.P)	20	25.1	6.3	33.3±3.3
	40	12.4	6.5	29.5±2.3
	80	6.3	8.3	22.2±2.2
	120	4.1	6	7.8±1.1
	160	3.1	6.8	6.5±5.5
	200	2.4	7.8	17.0±3.4
pH=3.35 TO 3.50				
Ni/Fe(3) (P.P)	20	277	7.2	15.5±2.2
	40	137	6.7	13.5±1.9
	80	69	5.3	10.0±3.5
	120	46	8.3	9.0±.1
	160	34	8.3	6.0±2.7
	200	27	5.8	4.1±.0
pH=3.35 TO 3.50				
Ni/Fe(3) (C.P)	20	25.1	8	22.4±5.5
	40	12.4	6.2	19.9±5.5
	80	6.3	7.2	17.3±12
	120	4.1	8.4	13.3±3.1
	160	3.1	5.9	5.3±7.3
	200	2.4	6.3	7.3±3.3
pH=3.35 TO 3.50				
Ni/Fe(4) (P.P)	20	277	8.3	13.7±7.5
	40	137	7.2	9.4±1.9
	80	69	7.9	7.3±4.2
	120	46	6.6	4.5±3.3
	160	34	6.3	3.3±2.3
	200	27	7.2	2.2±2.3
pH=3.35 TO 3.50				
Ni/Fe(4) (C.P)	20	25.1	8.2	17.7±2.1
	40	12.4	7.6	15.4±2.1
	80	6.3	6.7	8.9±3.3
	120	4.1	6.6	9.7±1.1
	160	3.1	6.4	9.7±2.2
	200	2.4	7.2	10.1±7.5

(P.P).indicates pulse-plating.

(C.P), indicates conventional-plating.

TABLE 16

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH AND FINALLY 'OFF'-TIME PERIOD TYPES OF PLATING UPON THE Ni/Fe DEPOSITS USING (EDAX)SCANNING ELECTRON MICROSCOPE TO DETERMINE THE NICKEL(%) AND IRON(Fe)%.

COATING THICKNESS=25um
USING 10 msec 'ON'
100 msec 'OFF'

CURRENT DENSITY mAcm-2	COPPER Cu%	HIGH pH 3.35,3.50		COPPER Cu%	LOW pH 2.5,2.80	
		IRON Fe%	NICKEL Ni%		IRON Fe%	NICKEL Ni%
Ni/Fe(1) SOLUTION						
20(P.P)	0.7	15.6	85.8	0.7	21.3	78.2
20(C.P)	0.3	28.9	67.6	0.3	36.5	60.5
80(P.P)	0.4	23.5	77.3	0.35	28.1	72.3
80(C.P)	0.4	29.3	64.4	0.35	38.2	60.1
200(P.P)	0.4	34.5	65.9	0.4	39	61.4
200(C.P)	0.3	37.9	61.3	0.24	40.1	58.8
Ni/Fe(2) SOLUTION						
20(P.P)	5.4	11.7	84.9	0.42	12.6	87.3
20(C.P)	0.5	25.3	72.4	0.95	31.4	69.9
80(P.P)	0.4	22.2	76.2	0.35	28.3	72.3
80(C.P)	0.4	27.2	63.5	2.4	35.5	60.0
200(P.P)	4.6	24.9	72.5	0.45	29.5	69.3
200(C.P)	0.6	13.9	87.7	0.6	15.3	79.3
Ni/Fe(3) SOLUTION						
20(P.P)	3.5	14.4	87.7	0.36	18.5	75.5
20(C.P)	1.2	22.3	71.3	0.36	24.5	69.5
80(P.P)	1.4	15	79.3	2.2	22.5	71.5
80(C.P)	2.4	19.3	72.5	2.1	29.5	68.1
200(P.P)	0.4	23.9	74.7	0.37	25.3	72.5
200(C.P)	0.3	17.1	82.5	0.33	27.3	65.5
Ni/Fe(4) SOLUTION						
20(P.P)	2.8	5.9	85.3	1.2	15.3	84.2
20(C.P)	0.3	3.4	97.1	1.8	21.4	75.2
80(P.P)	2.4	12.3	83.2	3.4	18.3	80.0
80(C.P)	1.8	8.5	89.6	2.7	13.5	85.5
200(P.P)	0.3	26.4	74.3	0.33	25	72.3
200(C.P)	0.3	1.7	98.1	0.33	12.3	82

(P.P), indicates pulse-plating.

(C.P), indicates conventional-plating.

TABLE 17

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, MEAN COATING THICKNESS, PLATING TIME, TYPES OF PLATING AND FINALLY THE 'OFF'-TIME PERIOD UPON NICKEL-IRON ALLOY AND WATTS DEPOSITS USING STRESSMETER TO DETERMINE THE MEAN STRESS IN THE ABOVE DEPOSITS.

COATING THICKNESS=25um
USING, 10msec 'ON' TIME
100msec 'OFF' TIME

SOLUTIONS	CURRENT DENSITY mAcm ⁻²	PLATING TIME (Min)	AVERAGE THICKNESS (um)	MEAN AVERAGE VALUE OF STRESS MNm ⁻² *10
pH=3.75 TO 4.0				
WATTS (P.P)	20	693.7	8.7	-13.5±26.2
	80	173.4	13.6	-10.67±16.4
	200	69	16.1	-3.5±1.7
WATTS (C.P)	20	63	24.1	-.4±.9
	80	15.5	17.5	.3±.2
	200	6.5	17.8	-7.9±3.4
pH=3.35 TO 3.50				
Ni/Fe(1) (P.P)	20	693.7	13.5	-5.2±1.5
	80	173.4	12.6	-14.0±19.1
	200	69	15.1	-7.3±7.9
Ni/Fe(1) (C.P)	20	63	14.2	-9.3±9.0
	80	15.5	17.1	-.9±0.8
	200	6.5	13	-2.5±2.6
pH=3.35 TO 3.50				
Ni/Fe(2) (P.P)	20	693.7	16.5	-3.2±6.1
	80	173.4	12.7	-22.9±12.4
	200	69	16.7	-3.9±1.8
Ni/Fe(2) (C.P)	20	63	17.9	-9.5±11.5
	80	15.5	17.6	-25.3±8.2
	200	6.5	17.2	-22.3±21.8
pH=3.35 TO 3.50				
Ni/Fe(3) (P.P)	20	693.7	15.2	-10.1±13.8
	80	173.4	14.8	-14.5±26.8
	200	69	16.3	-9.4±13.3
Ni/Fe(3) (C.P)	20	63	13.4	-59.8±21.9
	80	15.5	14.7	-22.5±27.3
	200	6.5	19.4	-14.8±6.9
pH=3.35 TO 3.50				
Ni/Fe(4) (P.P)	20	693.7	14.2	-10.5±3.7
	80	173.4	9.9	-30±43.5
	200	69	16.9	-12.9±14.3
Ni/Fe(4) (C.P)	20	63	13.2	-17.6±19.2
	80	15.5	20.9	-5.1±6.5
	200	6.5	18.9	-1.2±1.9

TABLE.18

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, TYPE OF PLATING (ONLY PULSE PLATING WAS APPLIED) UPON Ni/Fe DEPOSITS USING ATOMIC ABSORPTION SPECTROSCOPY TO DETERMINE NICKEL(Ni)% AND IRON(Fe)% .

COATING THICKNESS=10um

USING 10 msec 'ON'

200 msec 'OFF'

HIGH pH= 3.35,3.5

LOWpH=2.50,2.8

CURRENT DENSITY mAcm ⁻²	IRON Fe%	NICKEL Ni%	IRON Fe%	NICKEL Ni%
Ni/Fe(1) SOLUTION				
20(P.P)	9.7±3.4	90.3±4.9	18±3.7	82±.7
80(P.P)	29.1±2.7	70.9±2.1	35±2.1	65±4.4
200(P.P)	30±4.7	70±3.6	38.5±.7	61.5±3.7
Ni/Fe(2) SOLUTION				
20(P.P)	12±.2	88±5.2	27.5±2.1	72.5±2.9
80(P.P)	22.9±2.1	77.0±3.4	36.5±.7	63.5±2.2
200(P.P)	28±3.9	82.0±4.6	26±.3	74±2.5
Ni/Fe(3) SOLUTION				
20(P.P)	15.7±4.5	84.3±2.5	28.5±2.9	71.5±4.6
80(P.P)	18.5±4.2	81.5±3.7	27.5±2.6	72.5±4.2
200(P.P)	17±1.2	83±1.7	24.5±3.1	75.5±3.4
Ni/Fe(4) SOLUTION				
20(P.P)	8±2.1	92±2.9	11±2.1	89±3.7
80(P.P)	11±3.2	89±3.3	17.5±.7	82.5±2.9
200(P.P)	10±1.1	90±1.4	21±1.5	79±2.8

(P.P), indicates pulse-plating.

TABLE 19

EFFECTS OF PLATING PARAMETERS; CURRENT DENSITY, SOLUTION pH, TYPES OF PLATING (ONLY PULSE PLATING WAS APPLIED) AND FINALLY LONGER 'OFF'-TIME UPON THE Ni/Fe DEPOSITS USING ABSORPTION SPECTROSCOPY TO DETERMINE THE NICKEL (Ni)% AND IRON(Fe)%.

COATING THICKNESS=25um
USING 10 msec 'ON'
200 msec 'OFF'

CURRENT DENSITY mAcm ⁻²	HIGH pH=3.35-4.0		LOW pH=2.50-2.8	
	IRON Fe%	NICKEL Ni%	IRON Fe%	NICKEL Ni%
Ni/Fe(1) SOLUTION				
20(P.P)	17±4.5	83±3.41	29±3.75	71±2.71
80(P.P)	20±3.71	80±1.2	33±2.22	67±3.44
200(P.P)	19±2.75	81±.75	25.5±1.75	74.5±5.2
Ni/Fe(2) SOLUTION				
20(P.P)	12±1.23	88±2.11	23±1.27	77±1.27
80(P.P)	13±3.52	87±.5	17±3.77	83±4.41
200(P.P)	16±4.77	84±.9	19.5±2.22	80.5±3.2
Ni/Fe(3) SOLUTION				
20(P.P)	10±2.05	90±2.15	15.5±3.99	84.5±3
80(P.P)	9±1.11	91±2	12.77±4.5	87.23±3.
200(P.P)	11±.88	89±4.75	16.9±2.79	83.1±4.1
Ni/Fe(4) SOLUTION				
20(P.P)	5±1.25	95±3.25	9.5±1.23	90.5±2.2
80(P.P)	7±3.5	93±2.75	11.5±4.75	88.5±2.4
200(P.P)	8±1.77	92±3.95	18.8±2.12	81.2±3.2

(P.P), indicates pulse-plating.

FIGURE 1

Schematic representation of a square wave pulsed current.

FIGURE 2

Schematic representation of a square wave pulsed current with curved flow.

It does not show a pure square because there is a gradual curvature to both the ascending and descending current flow.

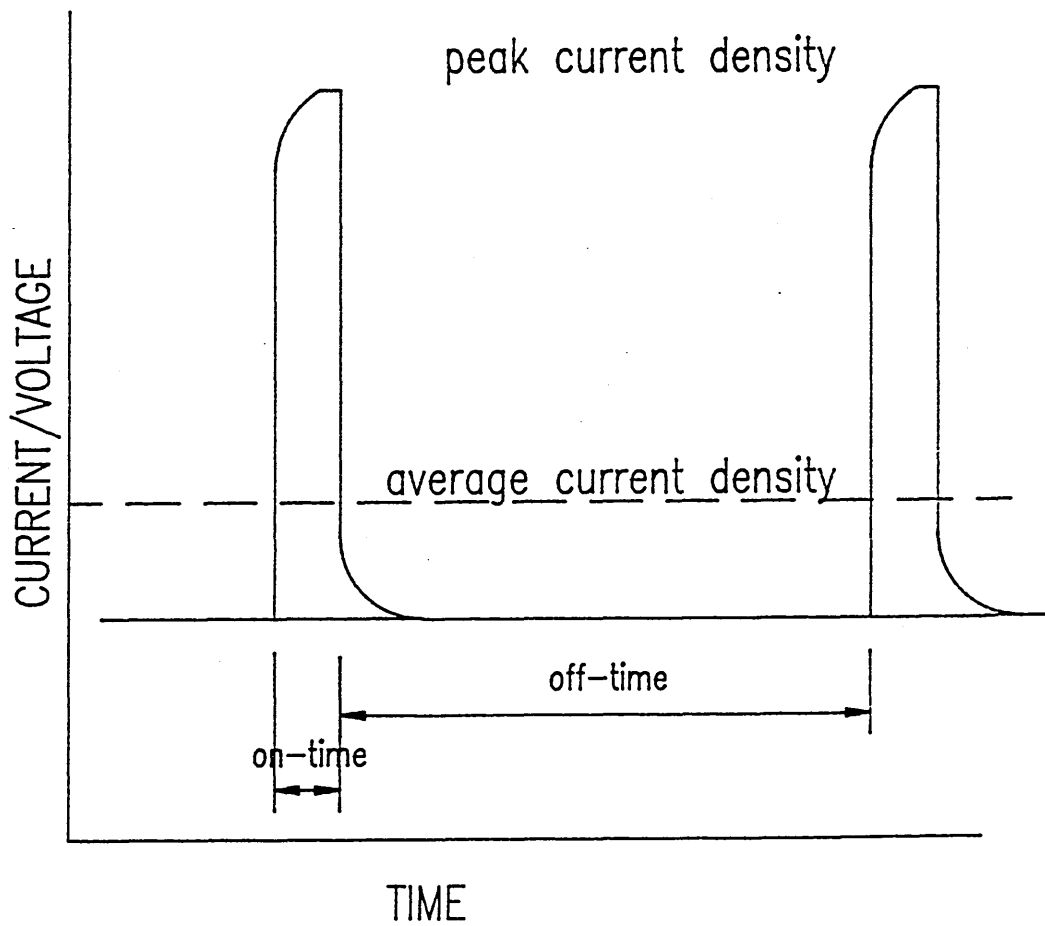
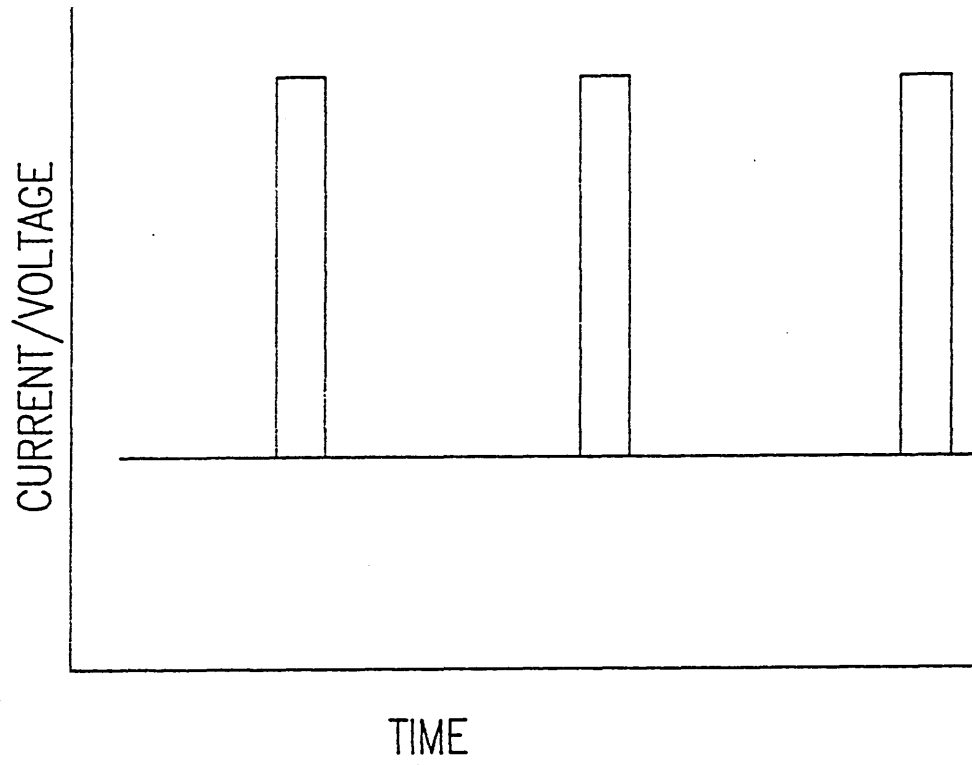


FIGURE 3

Schematic representation of the mechanism of potential difference across the cell due to the current source makes an excess of electrons available at the cathode.

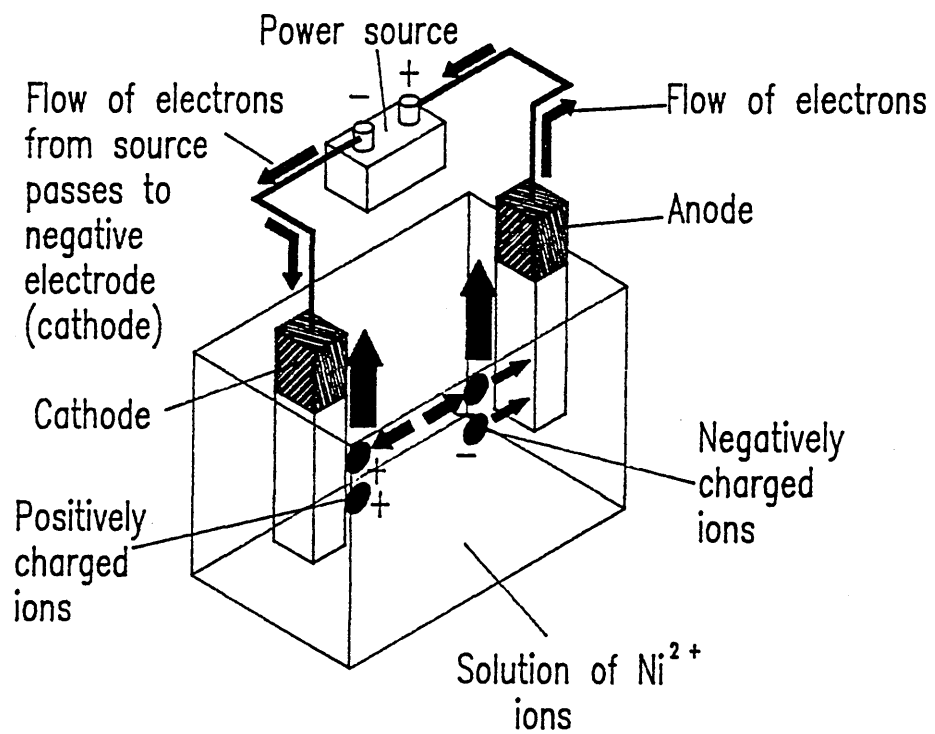


FIGURE 4

Schematic representation of the
mechanism of cathodic metal
deposition.

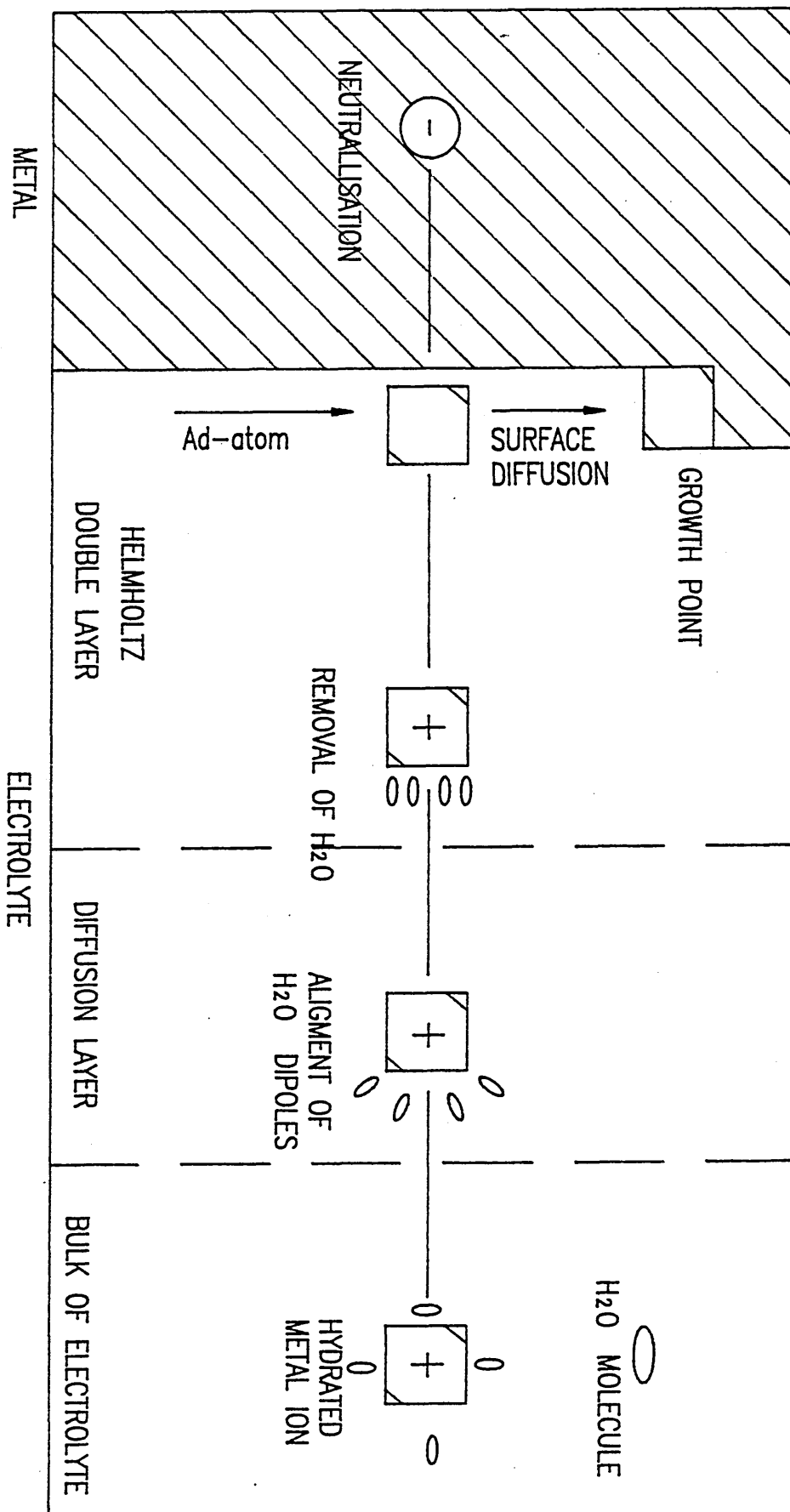


FIGURE 5

Illustration of three typical cases for two simultaneously deposited cations 'A' and 'B'.

Fig 5A. the two cathode potential-partial current density curves are far apart.

Fig 5B. represents the two cathode-current density curves close to each other.

Fig 5C. represents the two intersecting cathode potential-partial current density curves.

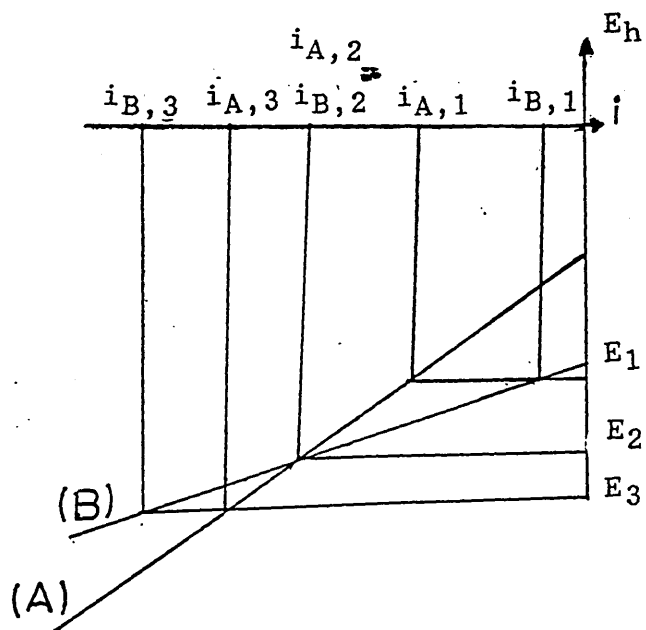
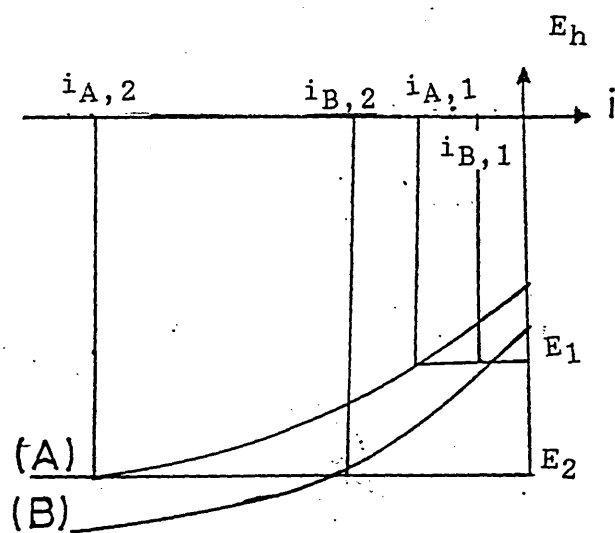
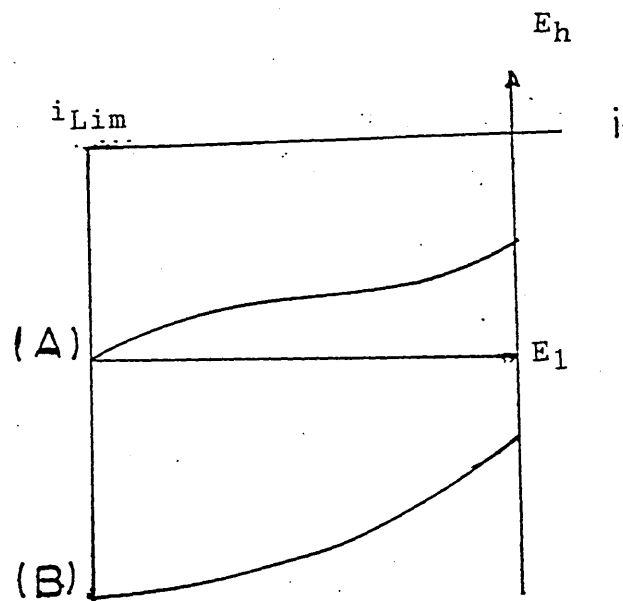


FIGURE 6

Representation of electrode potential-current density (polarisation) curves for copper and zinc ions.

Fig 6A. shows electrode potential-current density from sulphate electrolytes.

Fig 6B. shows electrode potential-current density from cyanide electrolytes.

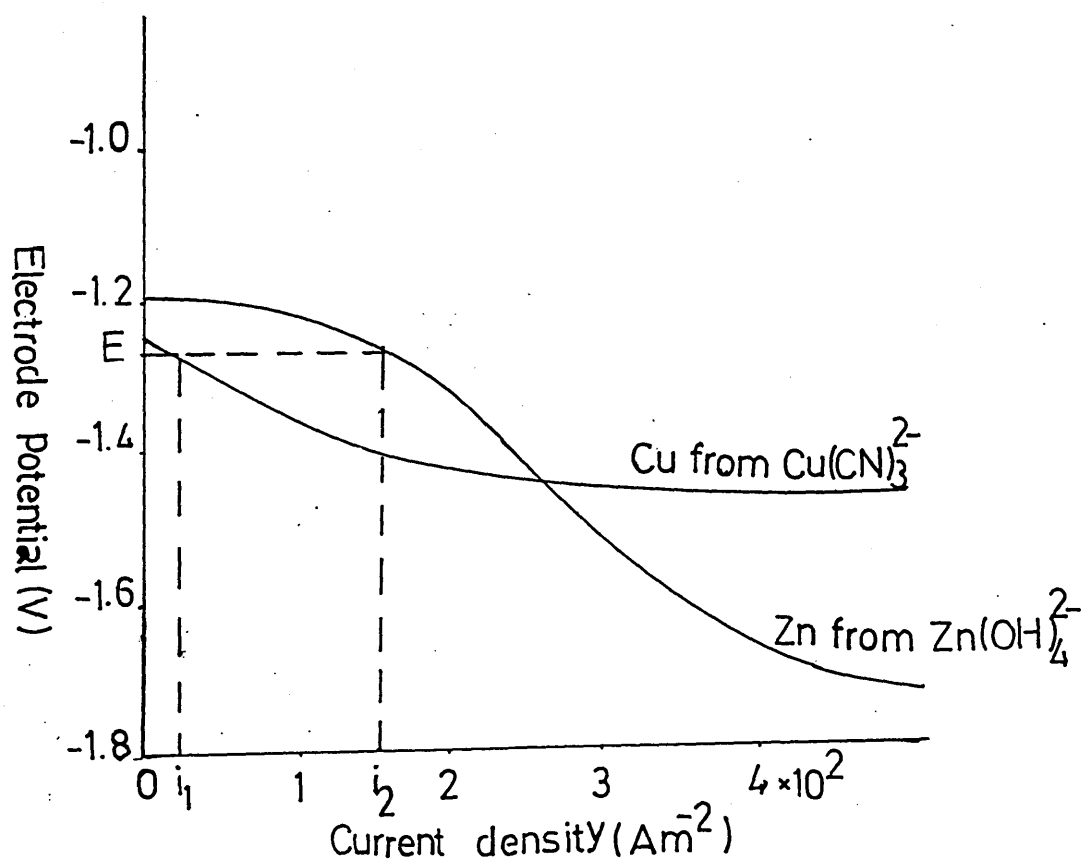
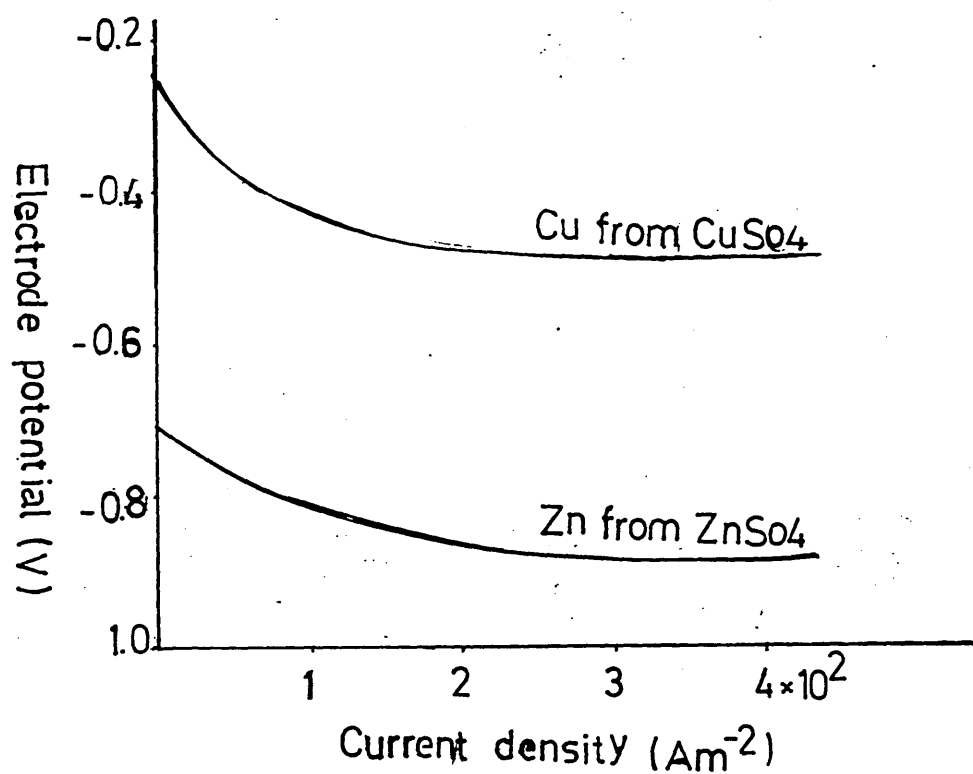
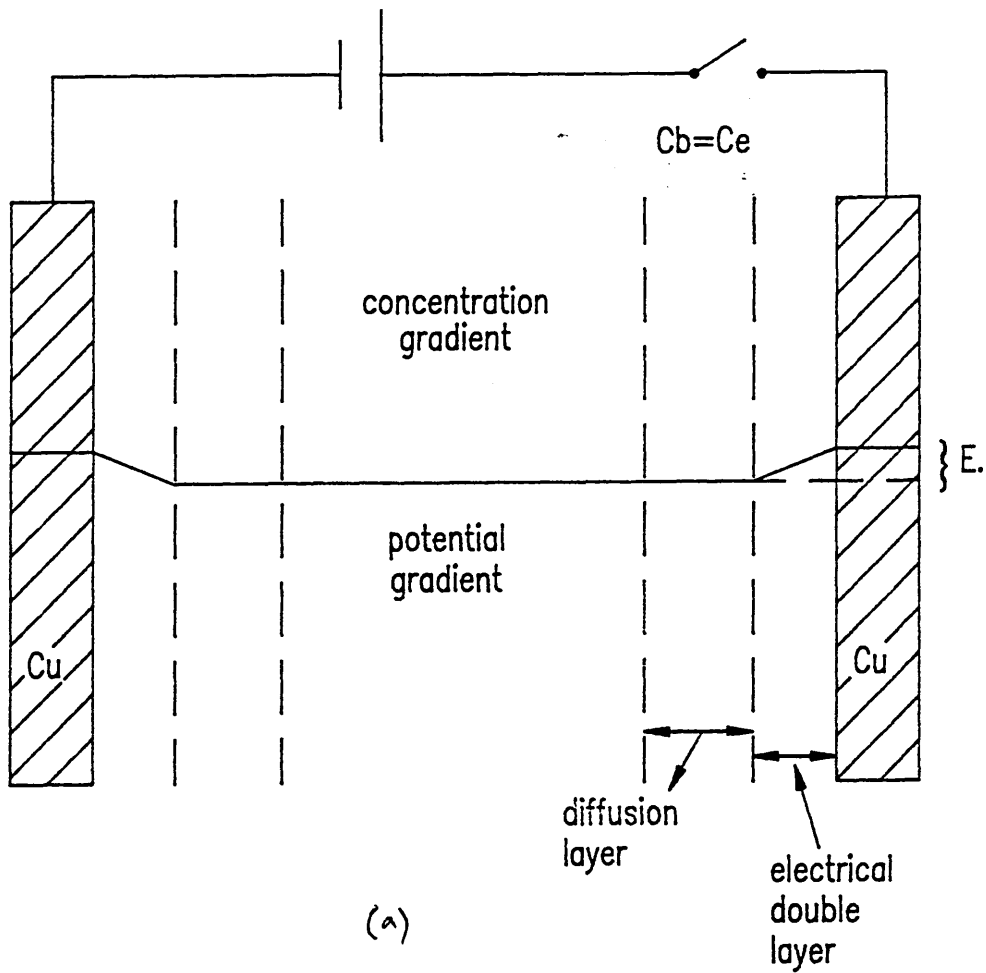


FIGURE 7

Potential and concentration gradients in the electrolytic cell $\text{Cu}/\text{CuSO}_4/\text{Cu}$.

(a) The electrodes are unpolarised; the potential difference is the equilibrium potential E_{eq} , and there is no concentration gradient in the diffusion layer.

(b) The electrodes are polarised; E_{eq} , whilst E_p of the cathode is more negative and concentration gradients exist across the diffusion layer; C_e , C_b are the concentrations at the electrode and in the bulk solution.



(a)

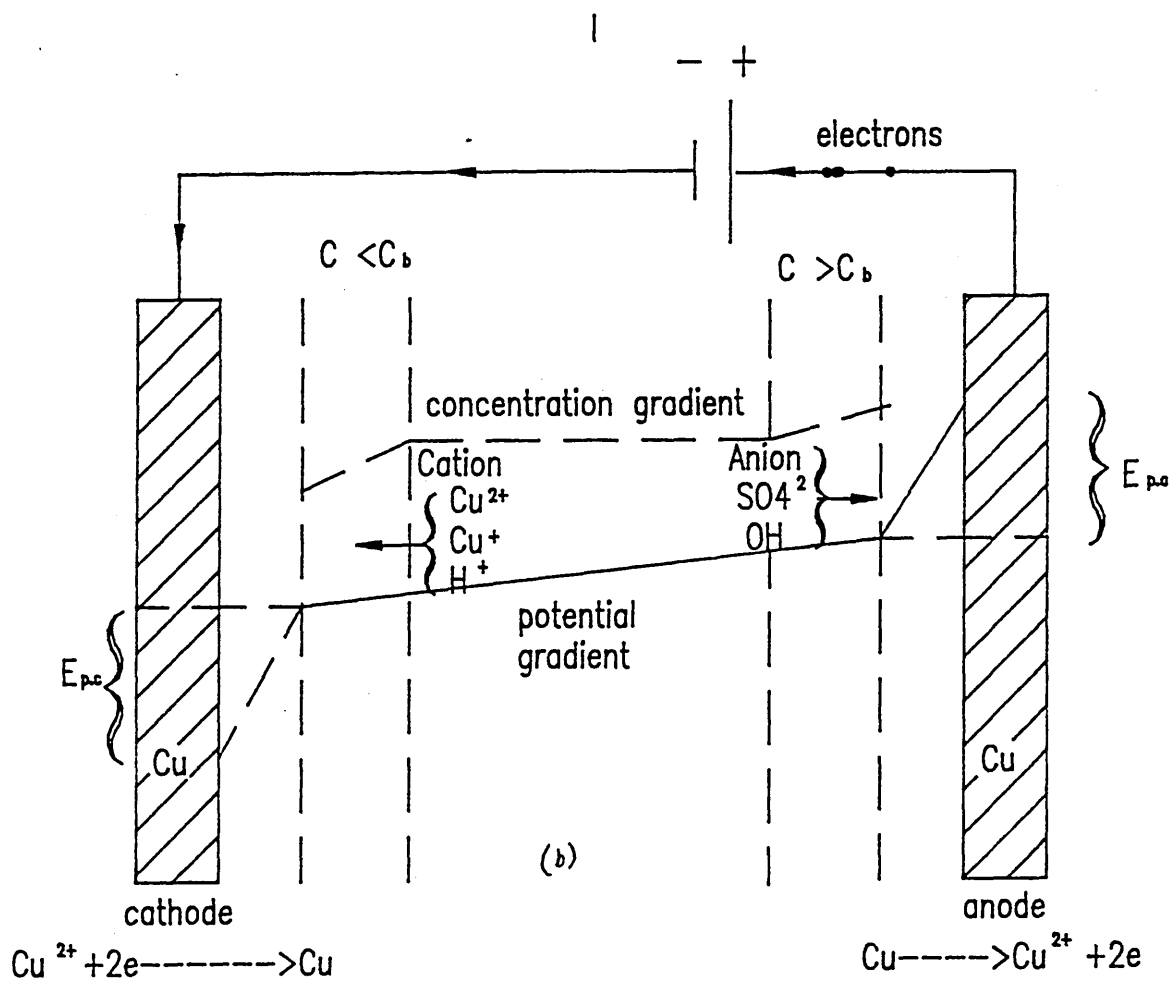


FIGURE 8

Schematic representation of the electrical double layer.

Double layer acts as a capacitor, with a fixed plate(the fixed layer) and a movable plate(the mobile layer).

FIGURE 8A

Schematic representation of the Helmholtz double layer(H.D.L) consisting of a plate of excess negative charges on the surface of the metal and a counterbalancing plate of excess positive charges(cations) in solution. The double layer as a whole being electrically neutral. The double layer can be regarded as equivalent to a capacitor in which the plates are separated by a distance.

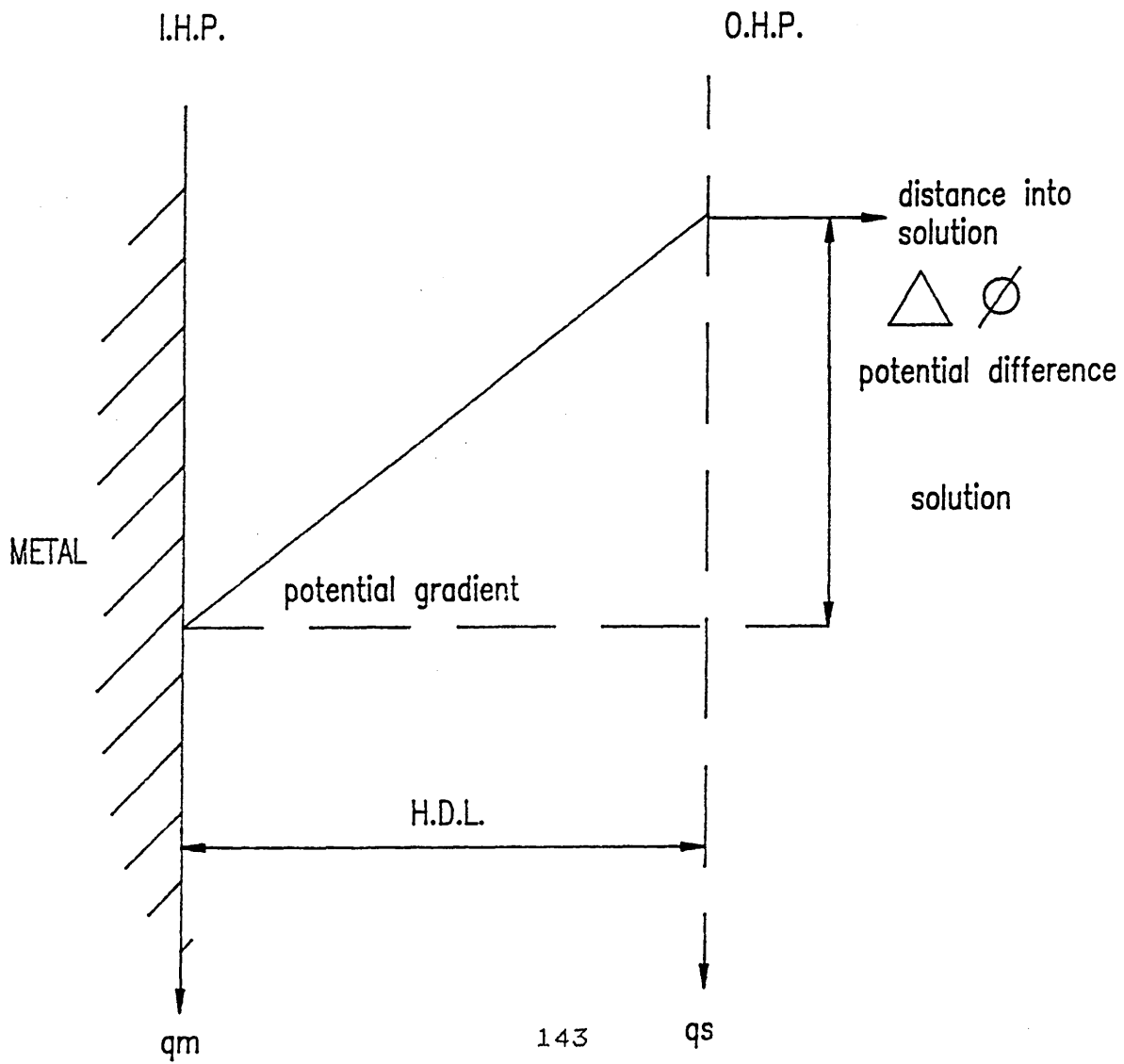
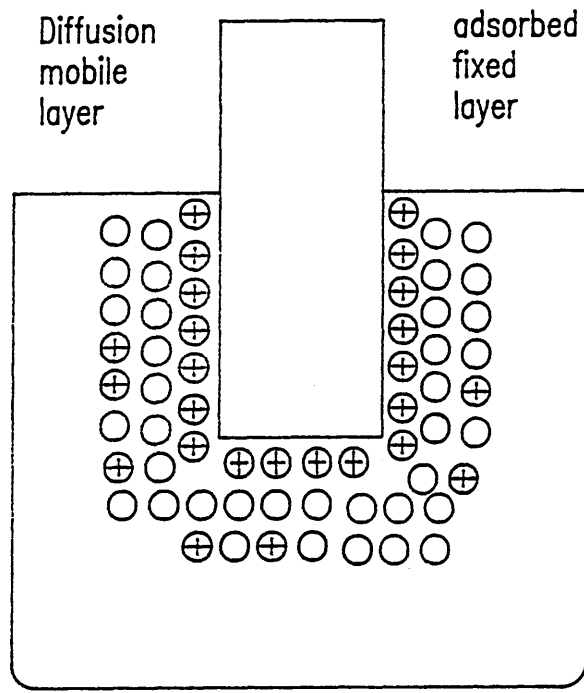
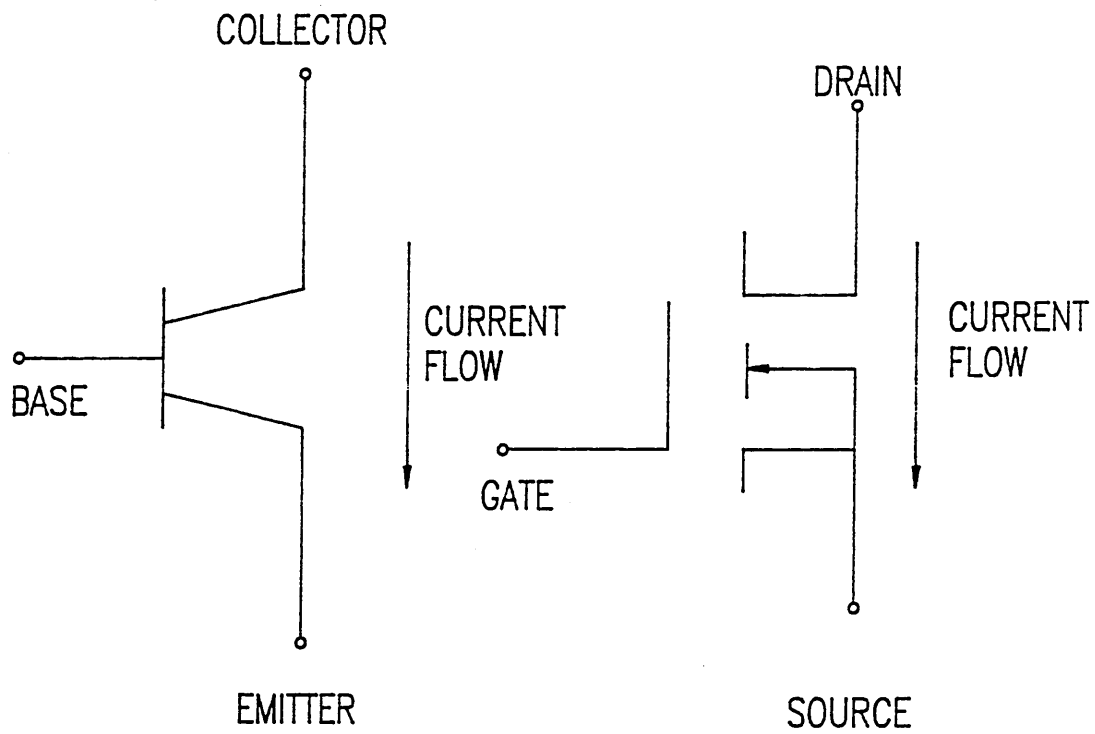


FIGURE 9

General view for bipolar and Mosfet electrical symbols. Instead of collector, emitter and base, electrical symbols for power Mosfets are; drain, source and base.



(a) NPN BIPOLAR TRANSISTOR

(b) N-CHANNEL MOSFET

FIGURE 10

Arrangement for the measurement of internal stress, using the EFCO-internal stressmeter with aid of copper coulometer bath.

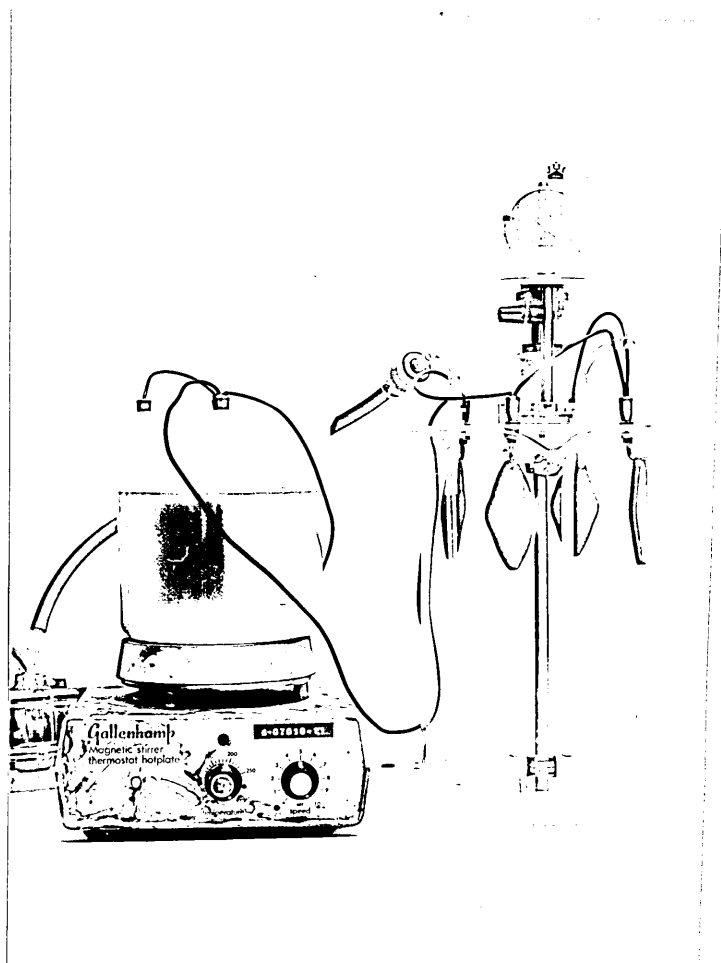


FIGURE 11

Schematic representation of the internal stressmeter (EFCO) which was used for continuous internal stress measurement. It is capable of measuring both tensile and compressive stresses of metal coatings to the same accuracy on a range of substrate materials.

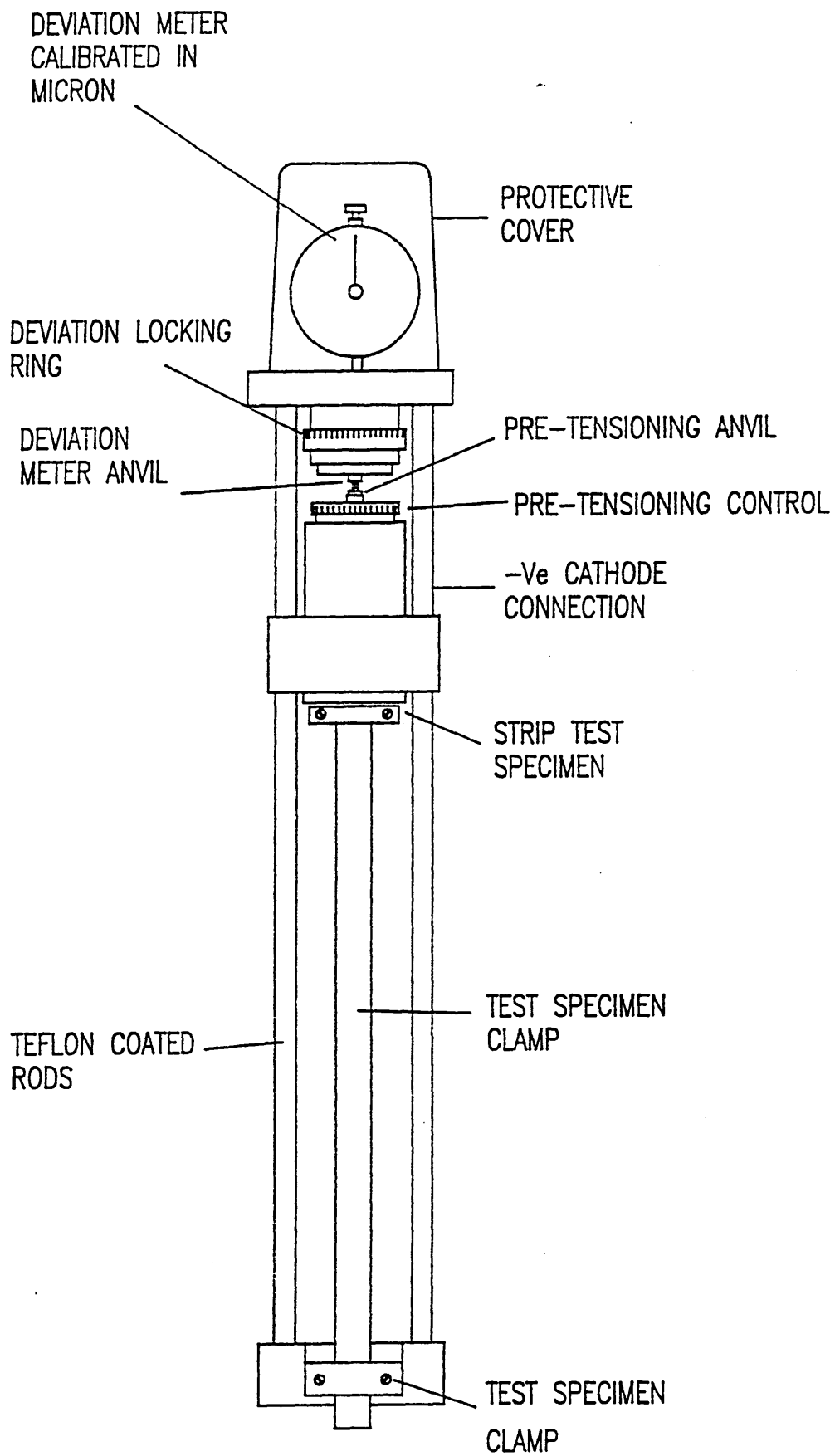


FIGURE 12

Schematic representation of the tensile test specimen which was used during Ni and Ni/Fe platings as a substrate. Copper was chosen due to have the same face centred cubic crystal(lattice-structure).

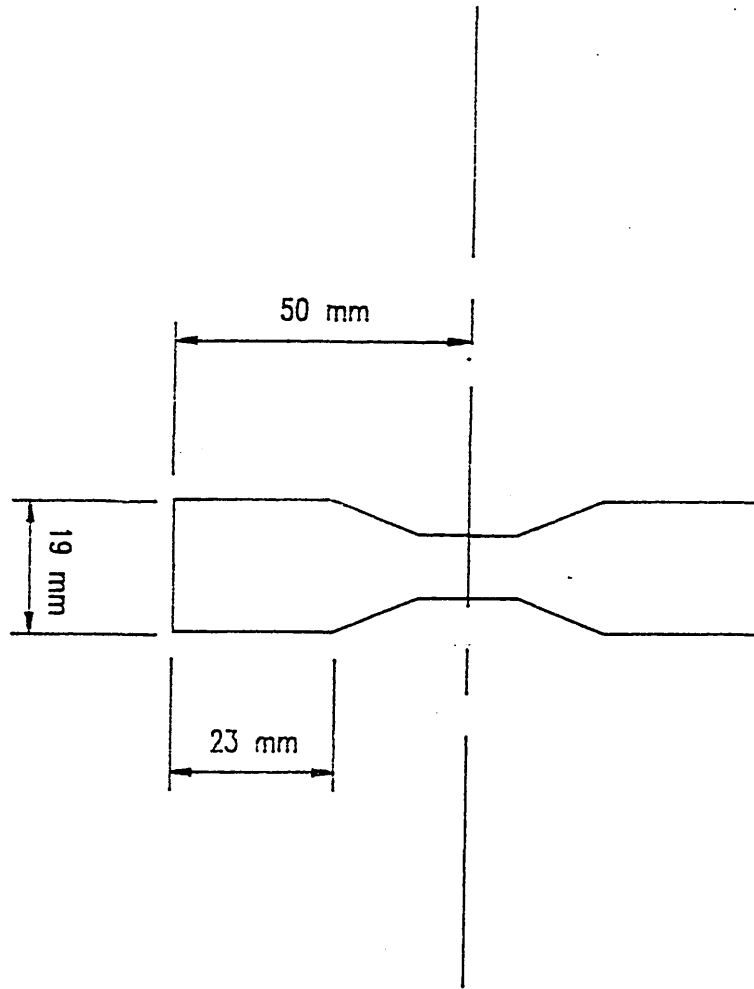


FIGURE 13

General view of Dummying process.
Two solutions were plated at the
same time with the corrugated
cathodes covered with anode bags
to prevent the solutions from
contamination.

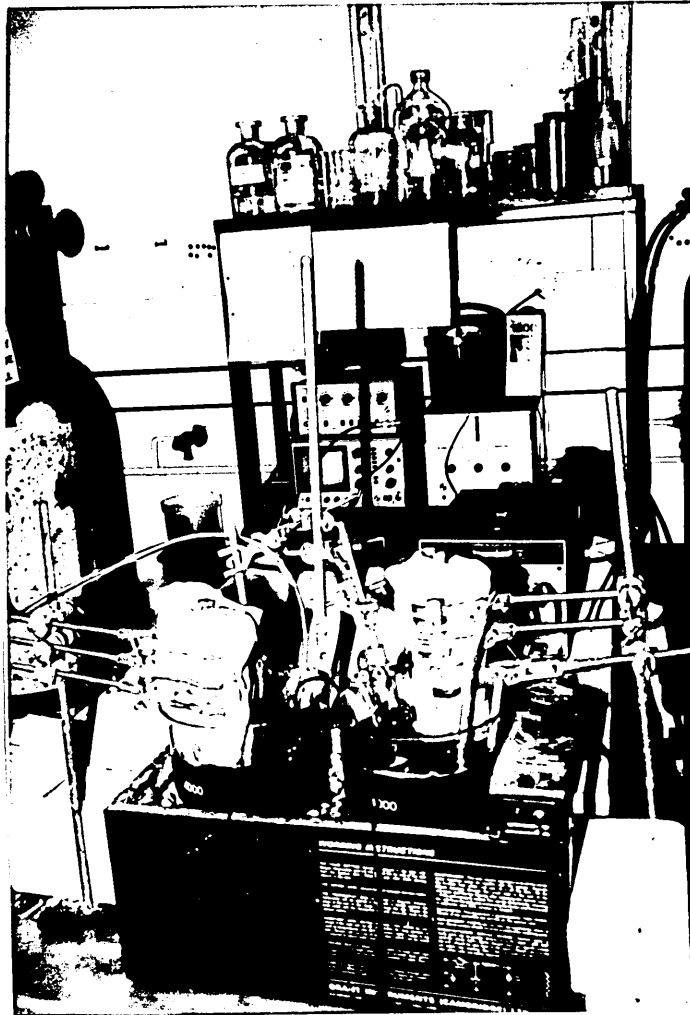


FIGURE 14

General view of pulse plating equipments (i) pulse generator, (ii) oscilloscope, (iii) power supply, (iv) power Mosfets and finally ammeter used during pulse plating.

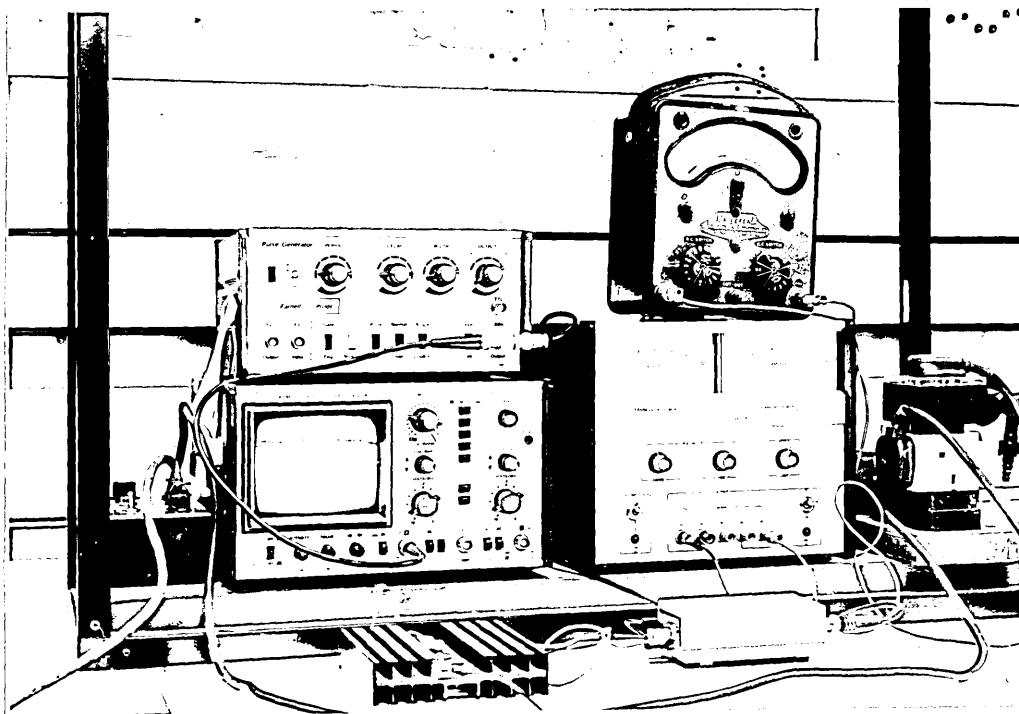


FIGURE 15

General view of normal plating cell and circuit showing plating bath, cathode cleaing cell, anodes with cotton bags to prevent any contamination in solution bath and finally the heating method.

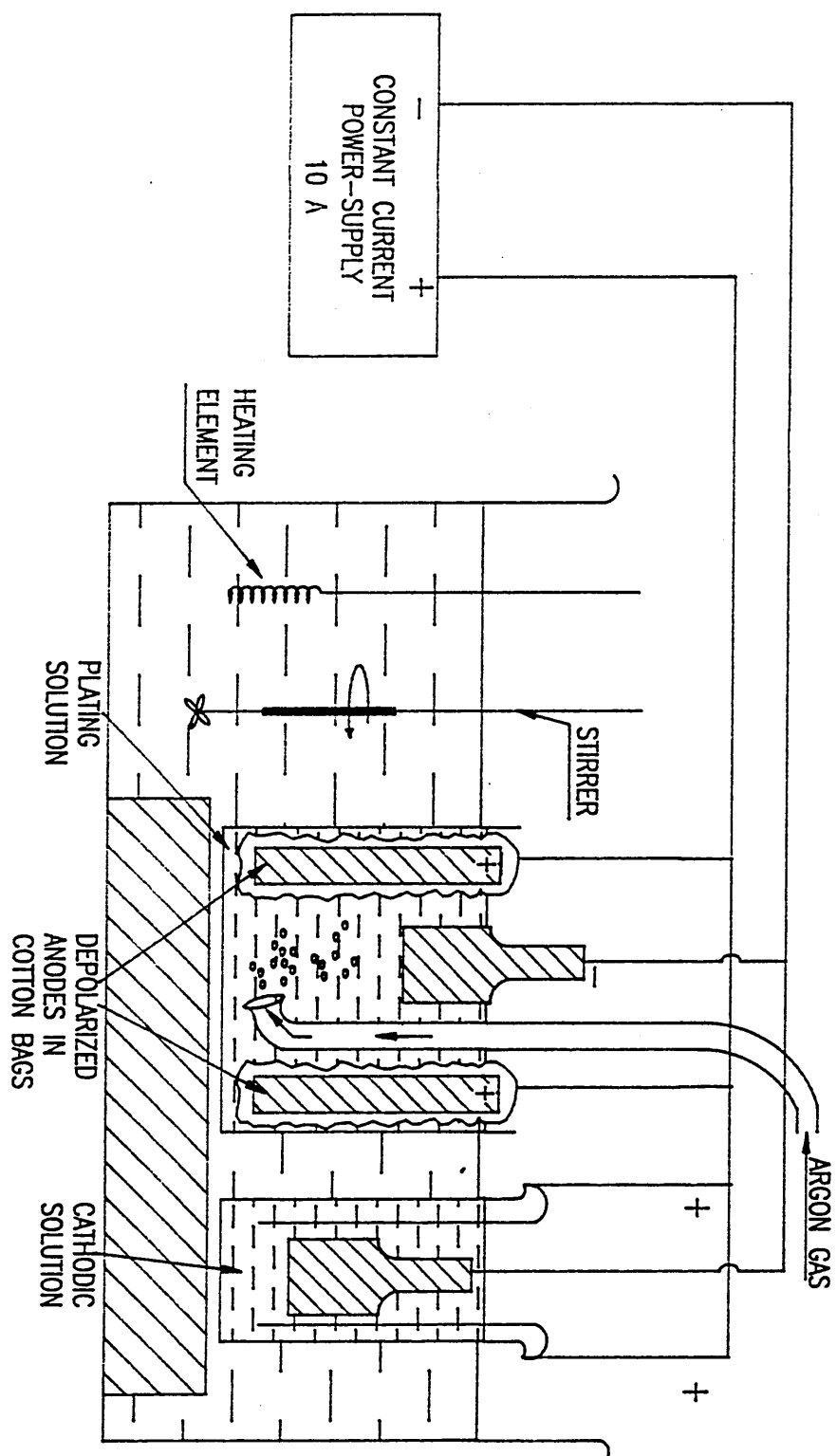


FIGURE 16

Surface appearances of well adhered and bright deposits resulting from Watts solution, using pulse-plating on copper substrate, plated at 20,40,80,120 and 200mAcm^{-2} current density corresponding to the numbers indicating(1,3,6,7,9) respectively.

FIGURE 17

Surface appearances of semi-bright reflective deposits resulting from nickel-iron(1) bath, using pulse plating on copper substrate, plated at 20,40,80,120 and 200mAcm^{-2} current density corresponding to the alphabetical numbers indicating (A,B,C,D,E) respectively.

FIGURE 18

Surface appearances of extremely bright and reflective deposits resulting from nickel-iron(4) bath , using pulse plating on cooper substrate, plated 20,40,80,120 and 200mAcm^{-2} current density corresponding to the numbers indicating (5,6,7,8,9) respectively.

FIGURE 19

Surface appearances of semi-bright and dull deposits resulting from Watts solution, using pulse-plating on mild-steel substrate, plated at 20,40,80 and 200mAcm⁻² current density corresponding to the alphabetical numbers indicating (A,B,D,E) respectively.

FIGURE 20

Surface appearances of semi-bright reflective deposits resulting from nickel-iron(2) bath, using pulse plating on mild-steel substrate, plated at 20,40,80 and 200mAcm⁻² current density corresponding to the alphabetical numbers indicating (A,B,D,E) respectively.

FIGURE 21

Effect of high current density on the 10um Watts deposits from Watts bath, using pulse plating. In early stage of experiments, adhesion was discovered with 200mAcm^{-2} current density; sample number(3). But with samples (1&2), lower current densities were applied.

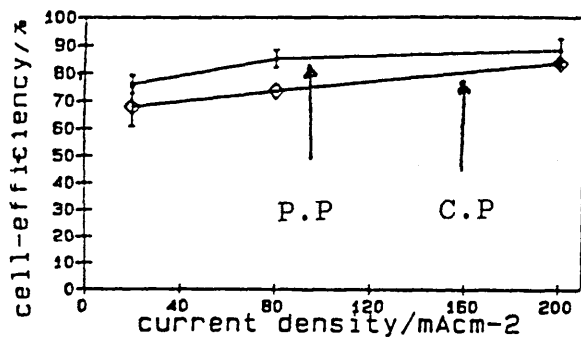
FIGURE 22

Variation of cell efficiency in the nickel/iron alloy and Watts deposits with effects of current density, solution pH and types of plating; pulse-plating(p.p), conventional-plating(c.p).

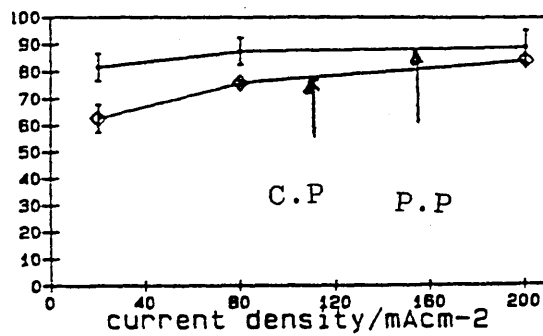
pH=3.35-3.50 for Ni/Fe and

pH=3.75-4.0 for Watts solutions
coating thickness=25um

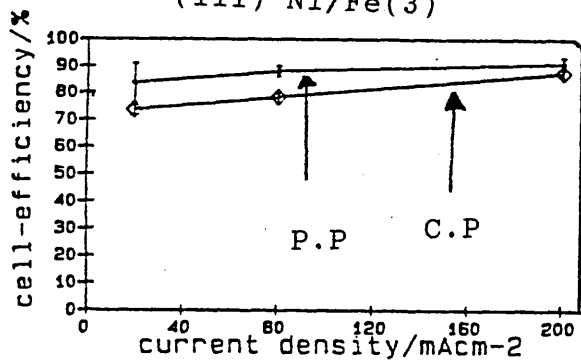
(i) Ni/Fe(1)



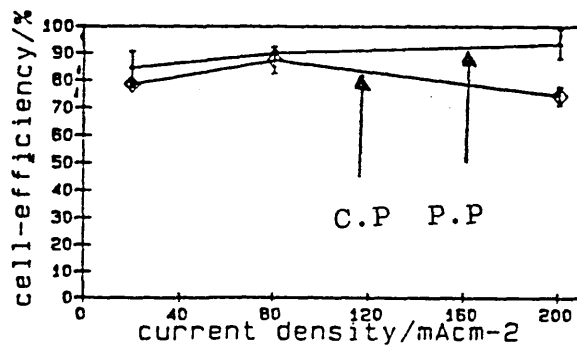
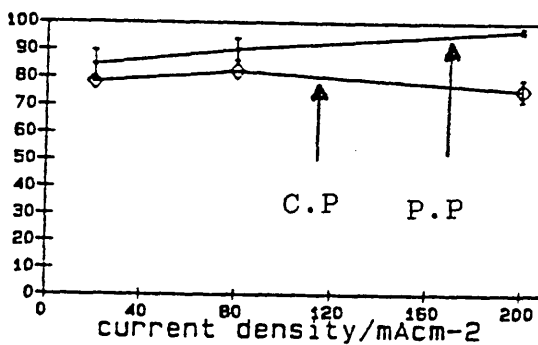
(i) Ni/Fe(2)



(iii) Ni/Fe(3)



(iv) Ni/Fe(4)



(v) WATTS

FIGURE 23

Mean internal stress of
nickel/iron and Watts deposits
with effects of current density,
solution pH and types of plating;
,pulse plating(p.p) ,convention-
al-plating(c.p).

pH=3.35-3.50 for Ni/Fe and

pH=3.75-4.0 for Watts solutions

coating thickness=10um

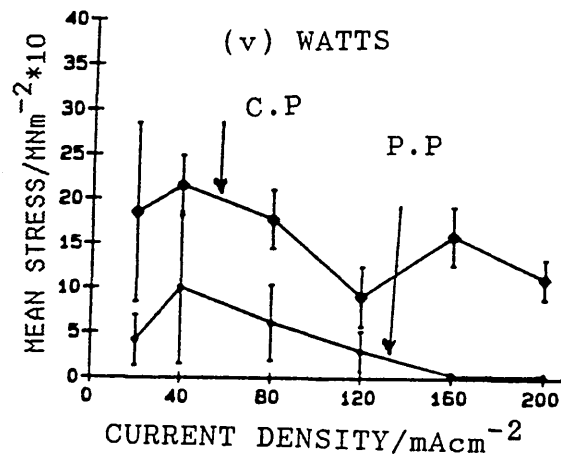
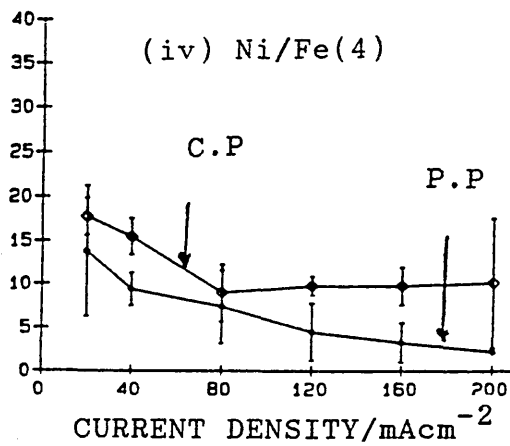
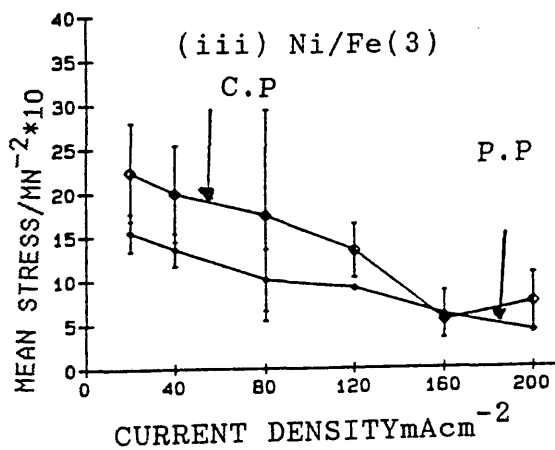
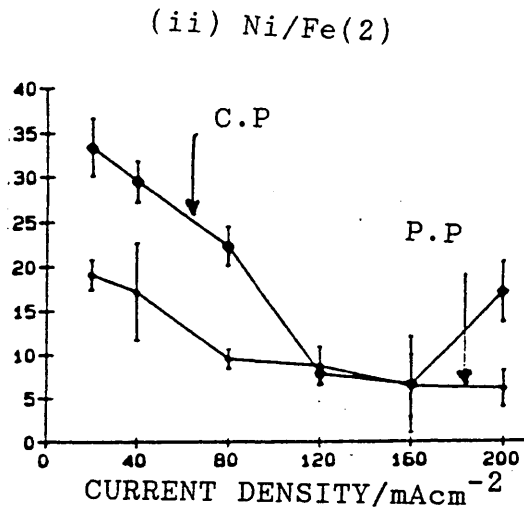
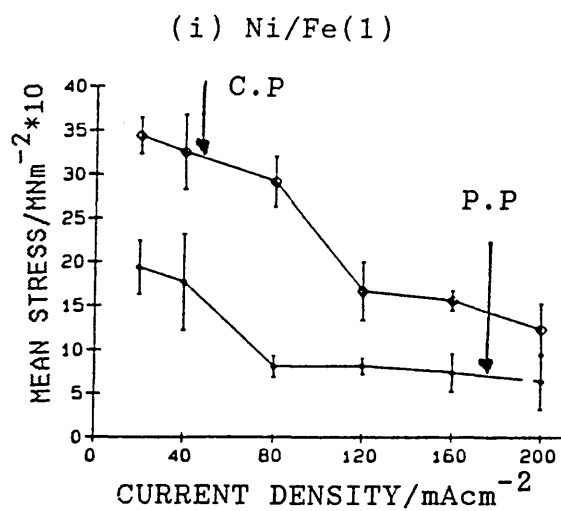


FIGURE 24

Variation of micro-hardness in the nickel/iron alloy and Watts deposits with effects of current density, solution pH and types of plating; pulse-plating(p.p), conventional-plating(c.p) and longer off-time period(l.o.t).

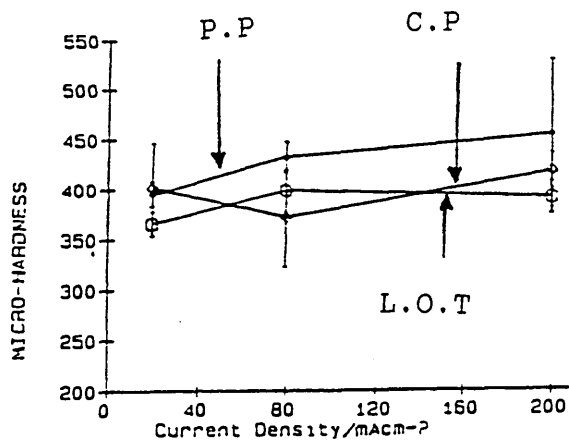
pH=3.35-3.50 for Ni/Fe and

pH=3.75-4.0 for Watts solutions

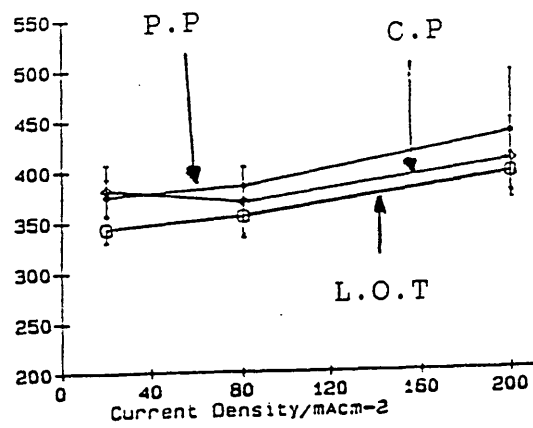
coating thickness=25um

off-time period=200msec

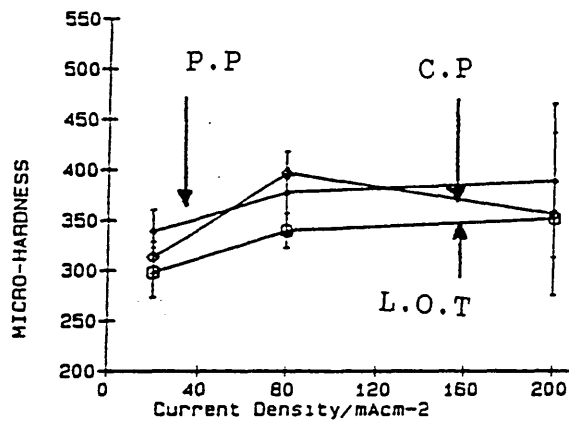
(i) Ni/Fe(1)



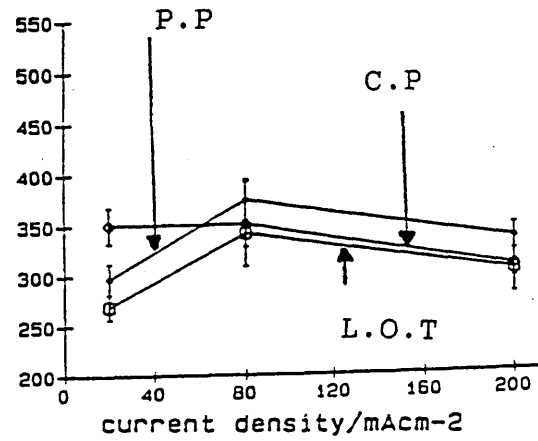
(ii) Ni/Fe(2)



(iii) Ni/Fe(3)



(iv) Ni/Fe(4)



(v) WATTS

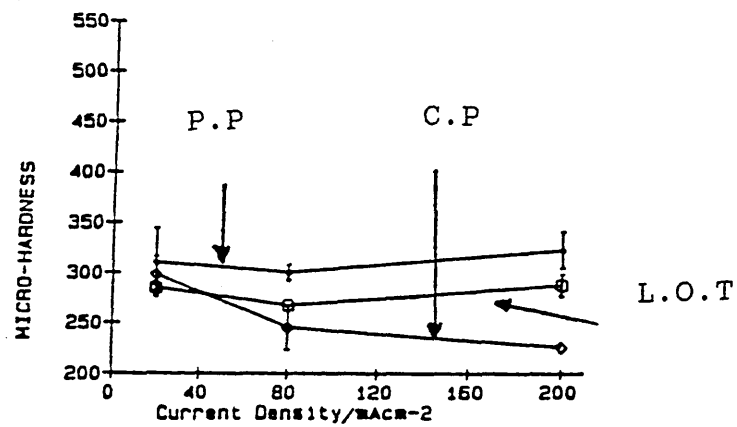


FIGURE 25

Surface appearances of dark and dull deposits resulting from Watts solution, using conventional-plating on copper substrate, plated at 20,40,80,120 and 200mAcm^{-2} current density corresponding to the alphabetical numbers indicating(A,H,J,T,U) respectively.

FIGURE 26

Surface appearances of semi-bright but not reflective deposits resulting from nickel-iron(1) bath, using conventional-plating on copper substrate, plated at 20,40,80,120 and 200mAcm^{-2} current density corresponding to the numbers indicating (1,2,3,4,5) respectively.

FIGURE 27

Surface appearances of bright but not reflective deposits resulting from nickel-iron(1)solution, using conventional-plating on copper substrate, plated at 20,40,80,120 and 200mAcm⁻² current density corresponding to the alphabetical numbers indicating , (P,Q,R,S,T) respectively.

FIGURE 28

Surface appearances of dark and dull deposits resulting from Watts solution, using conventional-plating on mild-steel substrate, plated at 20,40,80,120 and 200mAcm^{-2} current density corresponding to the numbers indicating (1,2,3,4,5) respectively.

FIGURE 29

Surface appearances of dull and dark deposits resulting from nickel-iron(2) bath, using conventional-plating on mild-steel substrate, plated at 20,40,80,120, 200 and 400mAcm^{-2} current density corresponding to the numbers indicating (1,2,3,4,5,6) respectively.

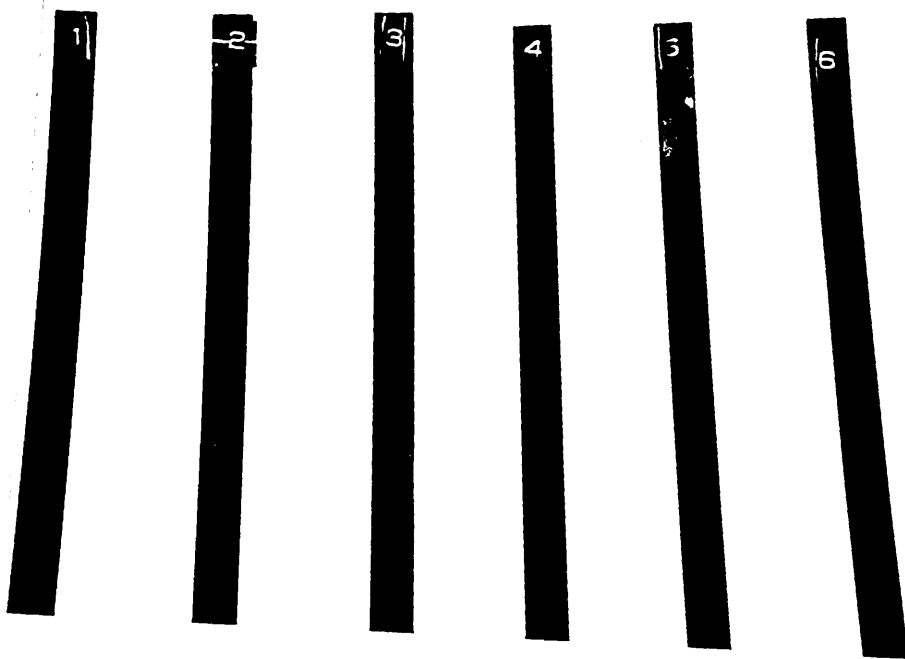
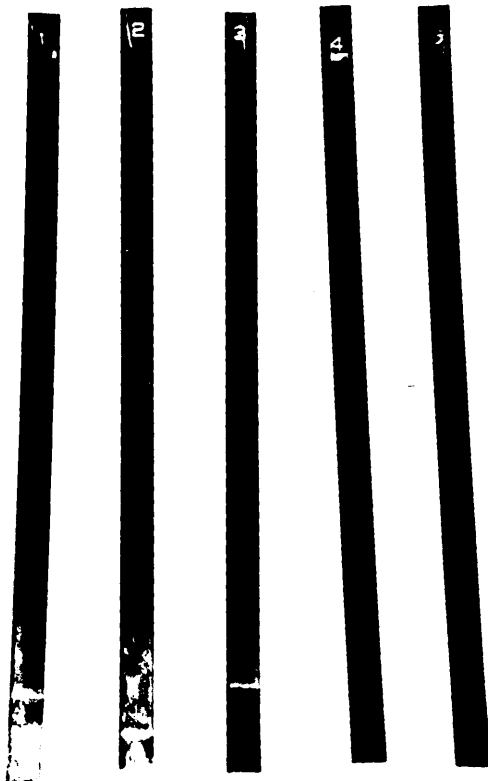


FIGURE 30

Effect of iron content on the
mean stress of the nickel-iron
alloy deposits, Ni/Fe(1).Ni/Fe(2)
,Ni/Fe(3) ,Ni/Fe(4) with effects
of iron, solution pH.
coating thickness=25um
pH=3.35-3.50

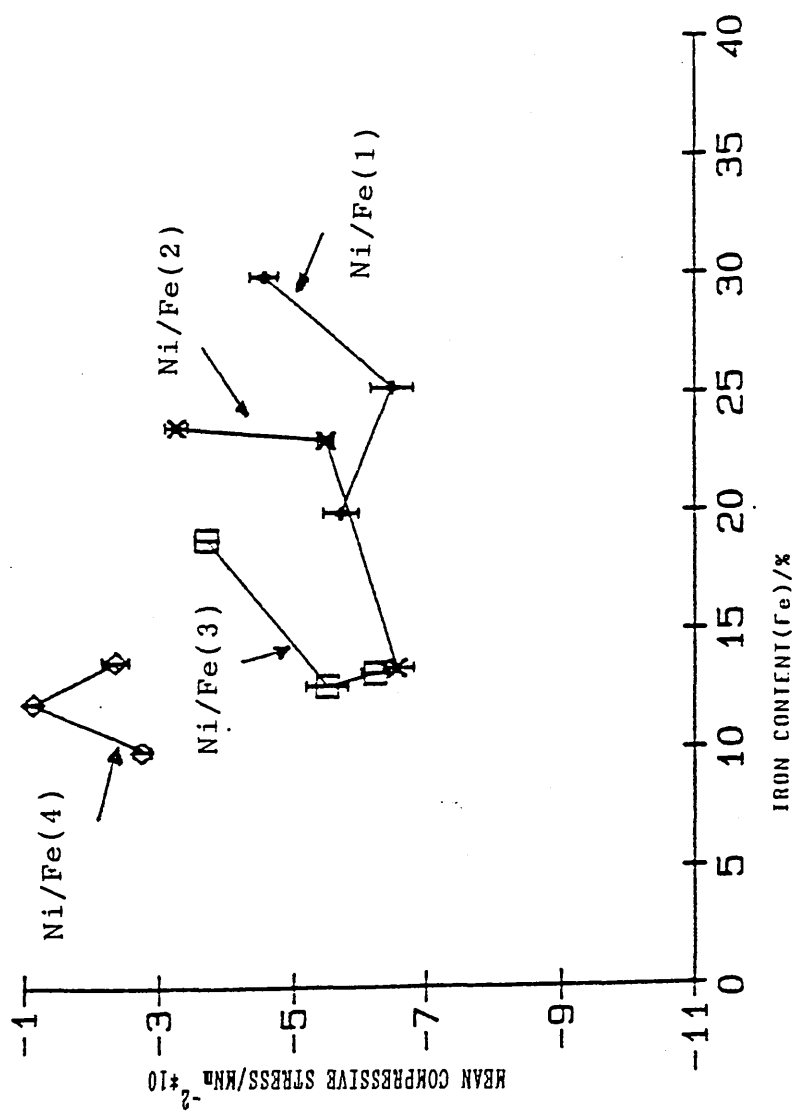


FIGURE 31

Variation of micro-hardness of
the nickel-iron alloy deposits ,
Ni/Fe(1), Ni/Fe(2), Ni/Fe(3),
Ni/Fe(4) with effects of iron,
nickel contents.

coating thickness=25um

pH=3.35-3.50

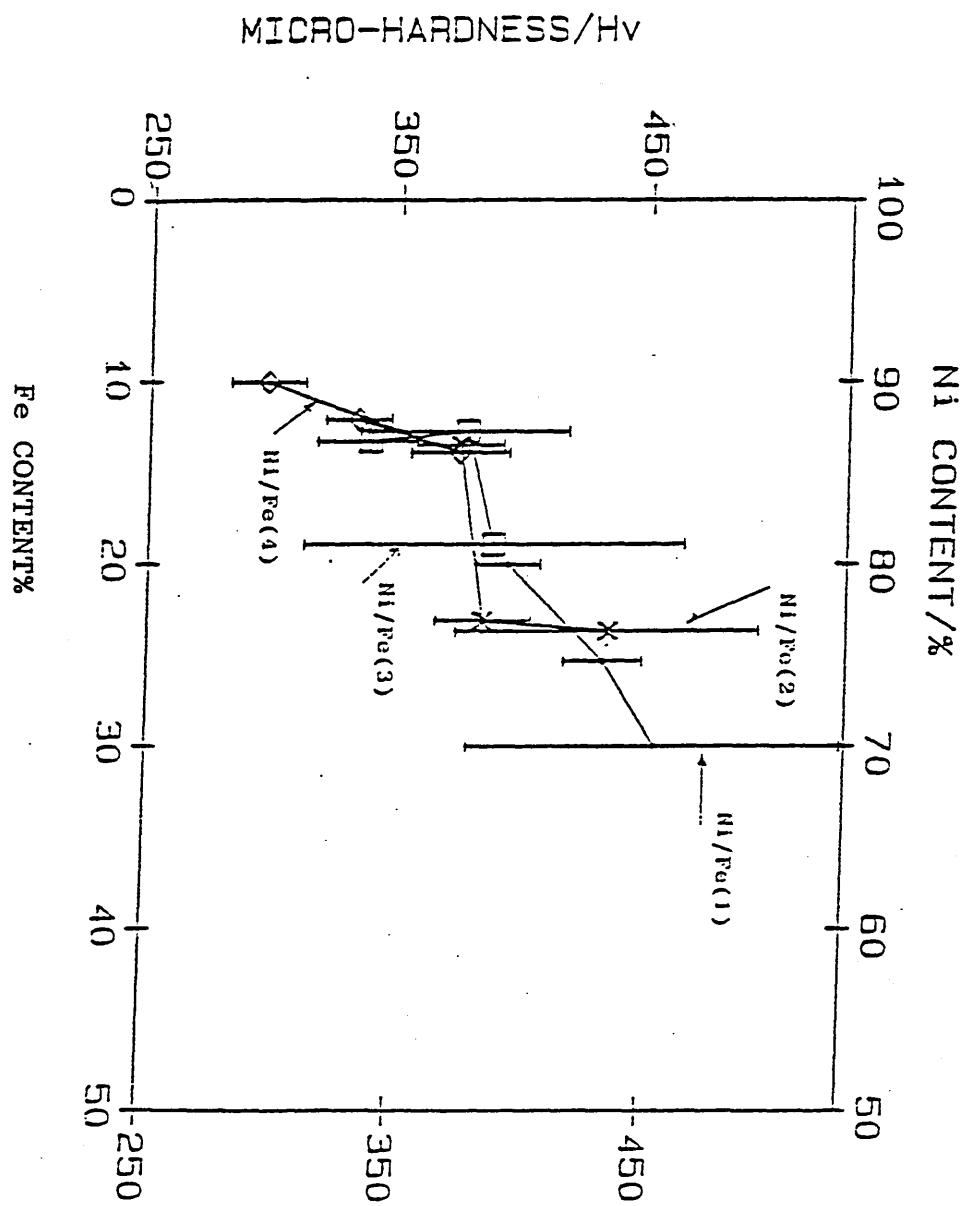
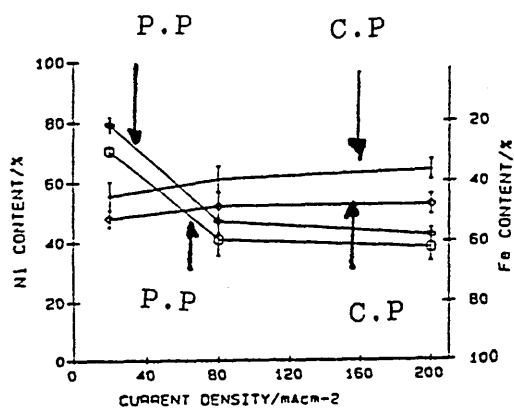


FIGURE 32

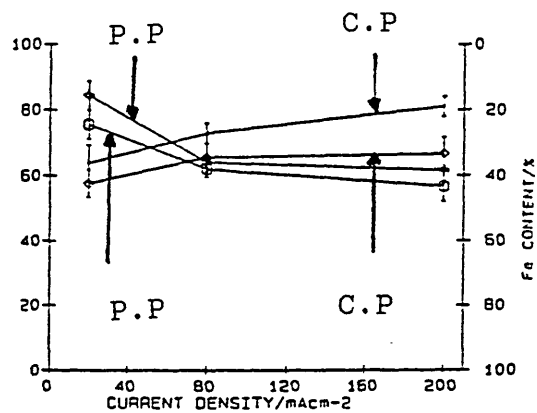
Composition of the nickel-iron alloy deposits with effects of current density, solution pH; (..higher pH, lower pH), types of plating; pulse and conventional plating and off-time period(O.T).

coating thickness=10um

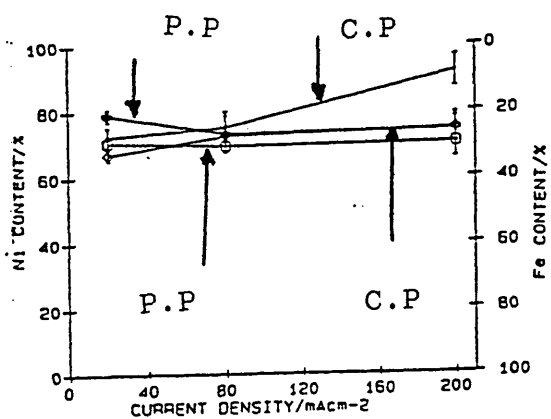
off-time period=100msec.



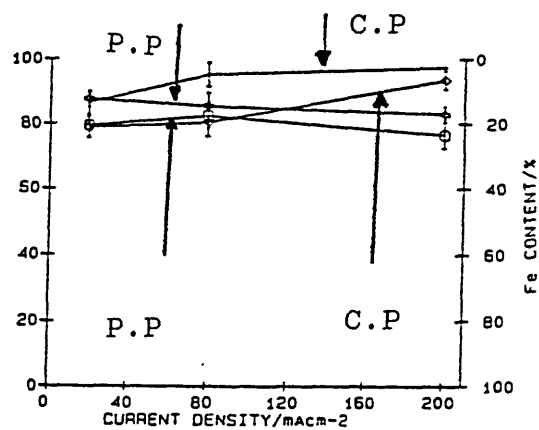
(i) Ni/Fe(1)



(ii) Ni/Fe(2)



(iii) Ni/Fe(3)



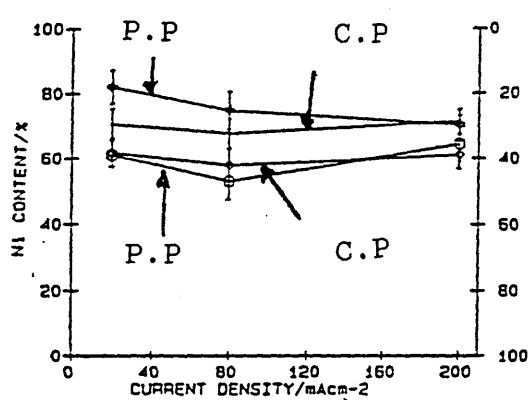
(iv) Ni/Fe(4)

FIGURE 33

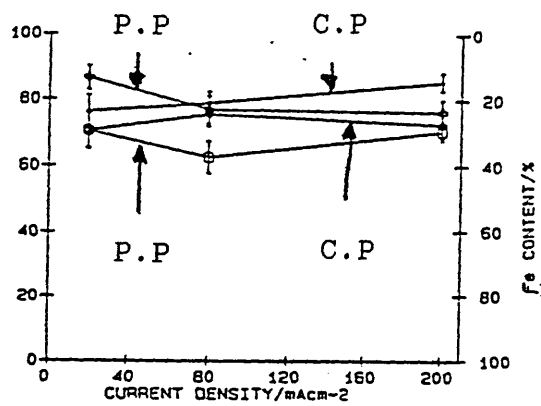
Composition of the nickel-iron alloy deposits with effects of current density, solution pH; (..higher pH, lower pH), types of plating; pulse and conventional plating and off-time period(O.T).

coating thickness=25um

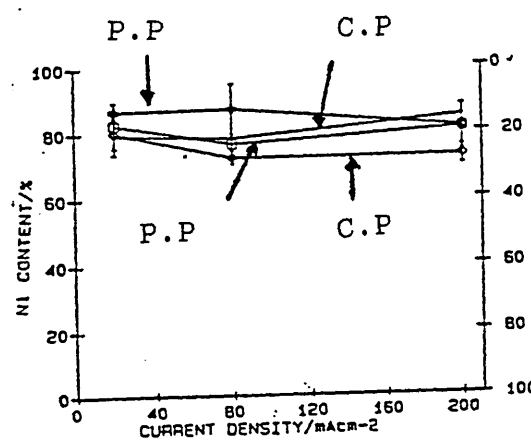
off-time period=100msec.



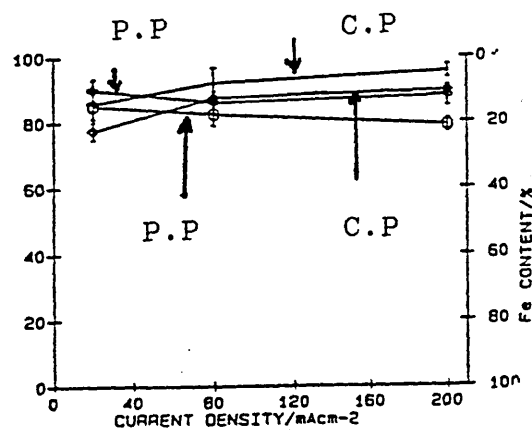
(i) Ni/Fe(1)



(ii) Ni/Fe(2)



(iii) Ni/Fe(3)



(iv) Ni/Fe(4)

FIGURE 34

Variation of micro-hardness of
the nickel-iron alloy deposits,
Ni/Fe(1) ,Ni/Fe(2) ,Ni/Fe(3) ,
Ni/Fe(4) with effects of iron,
nickel contents, solution pH;
(lower pH).

coating thickness=25um

pH=2.5-2.8

MICRO-HARDNESS/Hv

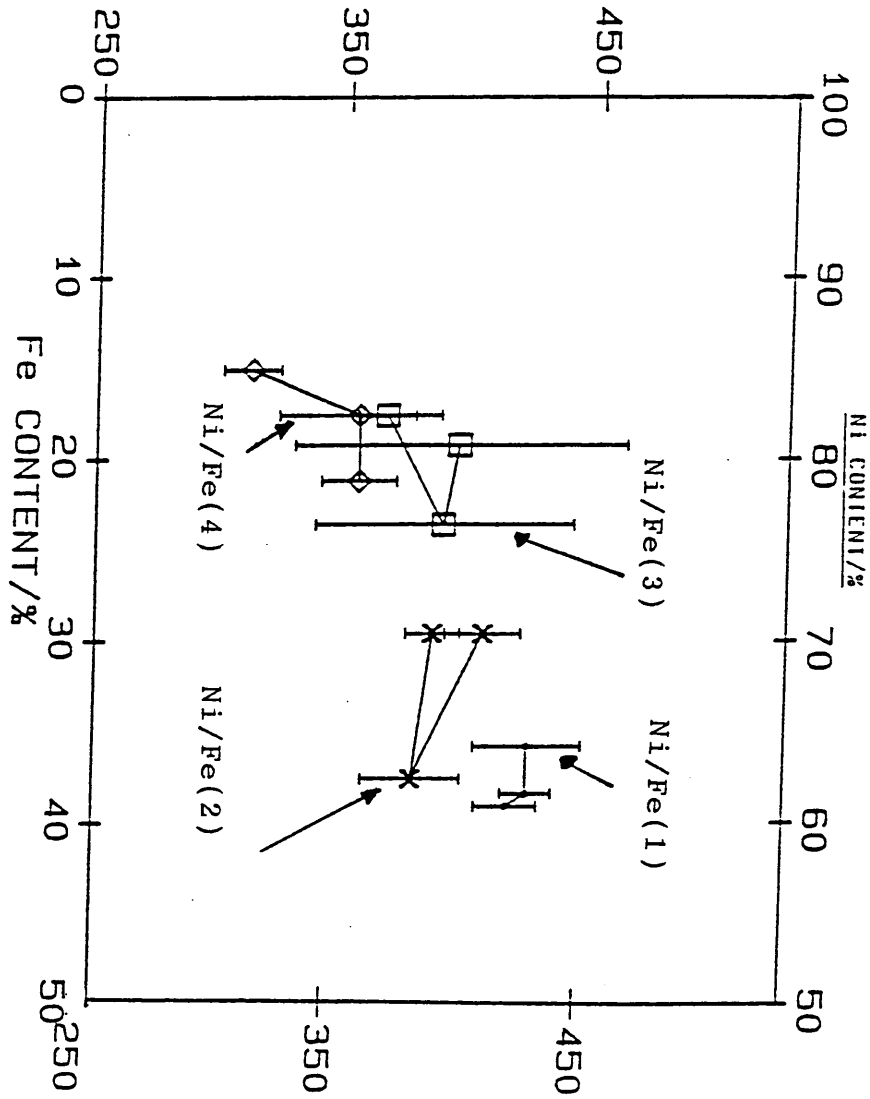


FIGURE 35

Variation of micro-hardness in the nickel/iron alloy and Watts deposits with effects of current density, solution pH and types of plating, pulse-plating(p.p), conventional-plating(c.p) and longer off-time period(l.o.t).

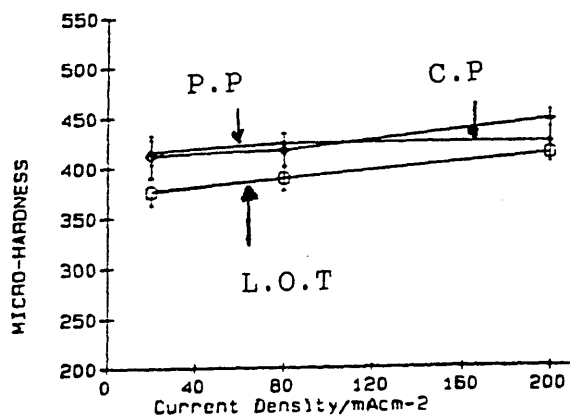
pH=2.5-2.8 for Ni/Fe and

pH=3.30-3.55 for Watts solutions

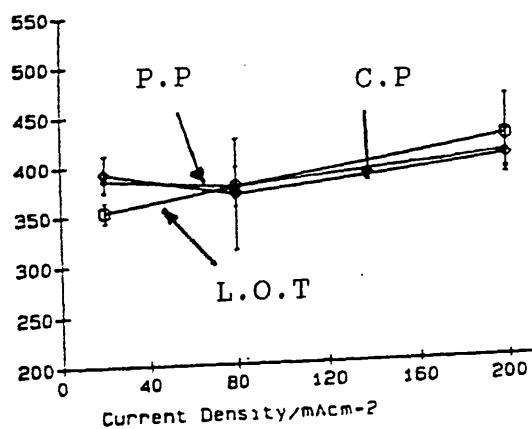
coating thickness=25um

off-time period=200msec

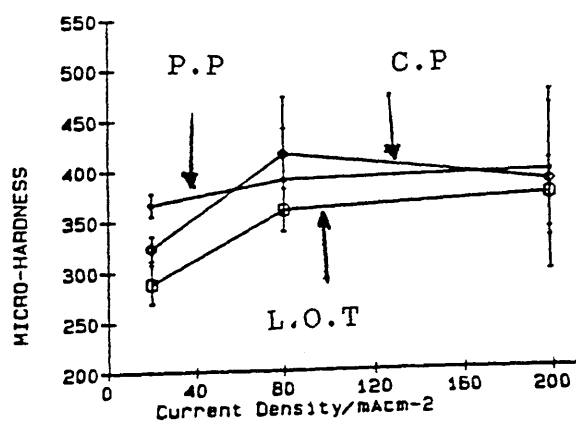
(i) Ni/Fe(1)



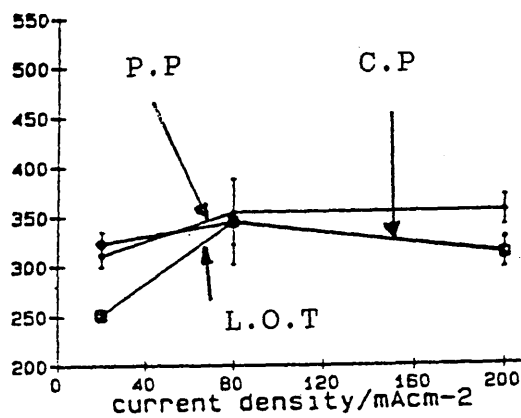
(ii) Ni/Fe(2)



(iii) Ni/Fe(3)



(iv) Ni/Fe(4)



(v) WATTS

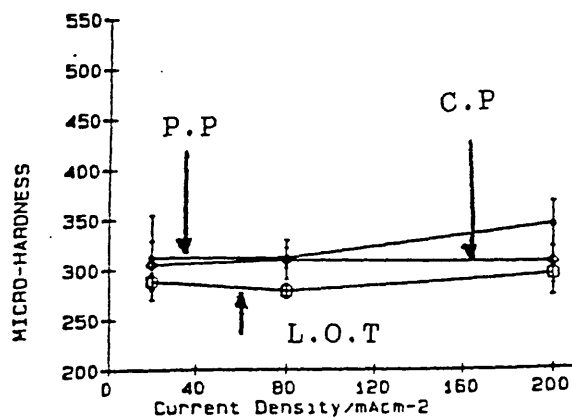


FIGURE 36

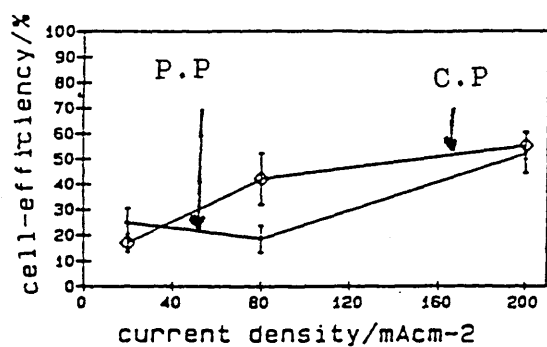
Variation of cell efficiency in the nickel/iron alloy and Watts deposits with effects of current density, solution pH and types of plating, pulse-plating(p.p), conventional-plating(c.p).

pH=2.5-2.8 for Ni/Fe and

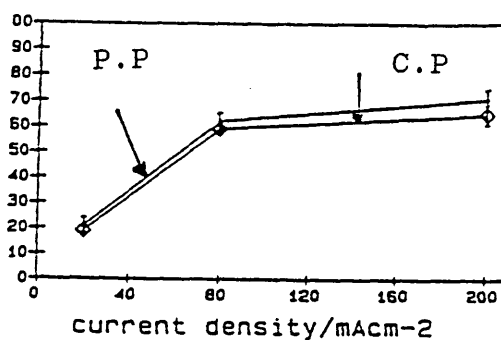
pH=3.30-3.55 for Watts solutions

coating thickness=25um

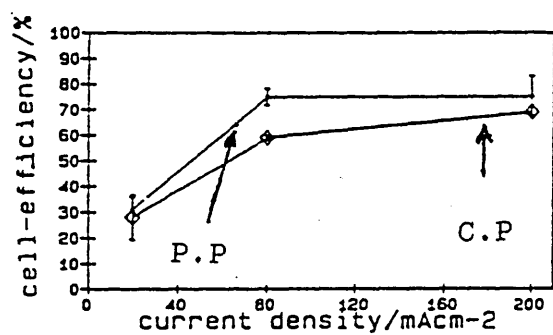
off-time period=200msec



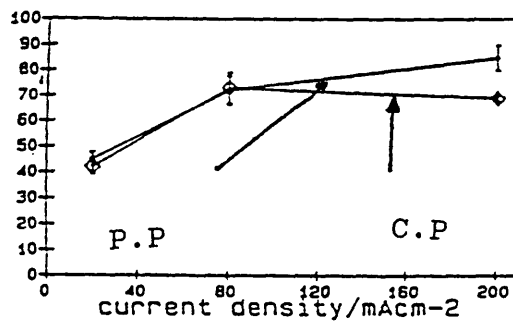
(i) Ni/Fe(1)



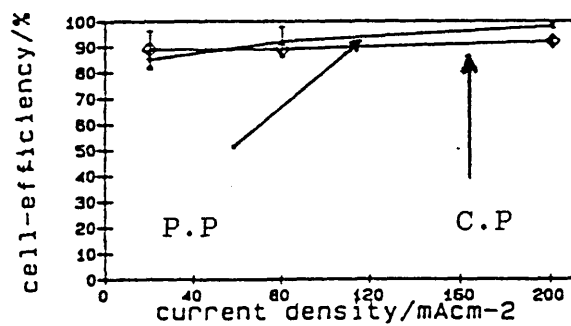
(ii) Ni/Fe(2)



(iii) Ni/Fe(3)



(iv) Ni/Fe(4)



(v) Watts

FIGURE 37

Effect of plating conditions on the 10um Watts deposits from Watts bath, using conventional-plating(c.p) and low pH value. samples (1,2&3) represent the 20,120&200mAcm⁻² current densities .These samples are badly peeled-off and consequently stress measurements within samples are meaningless.

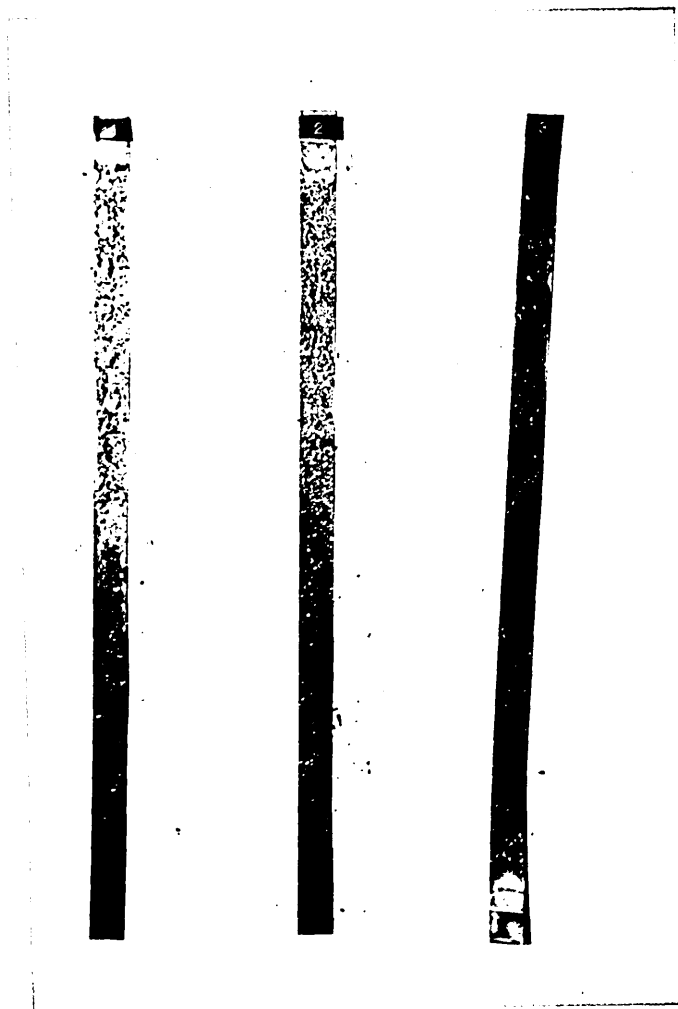


FIGURE 38

X-ray measurements of mean stress
in the nickel/iron alloy and
Watts deposits with effects of
current density, solution pH and
types of plating, pulse plating
, conventional-plating(c.p) .

pH=2.5-2.8 for Ni/Fe and

pH=3.25-3.55 for Watts solutions

coating thickness=25um

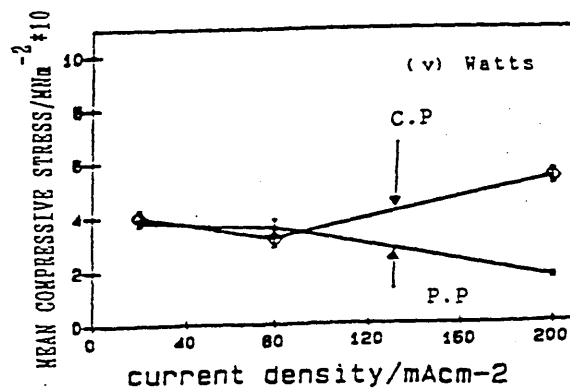
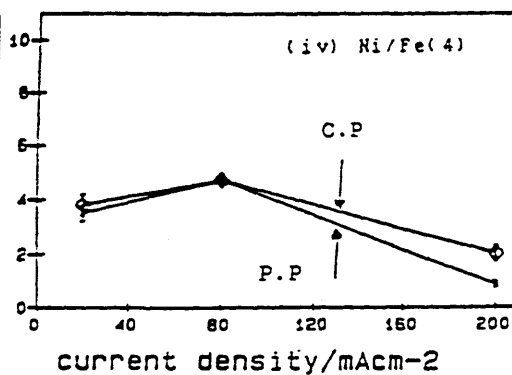
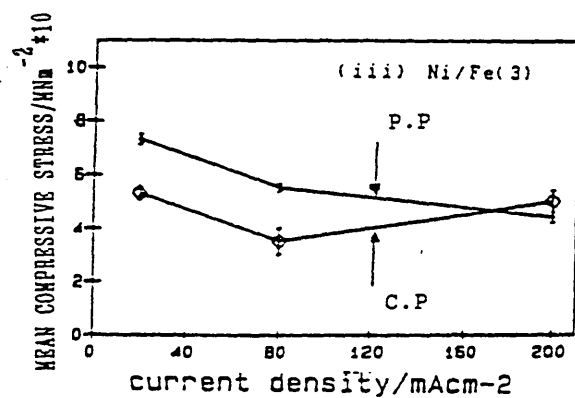
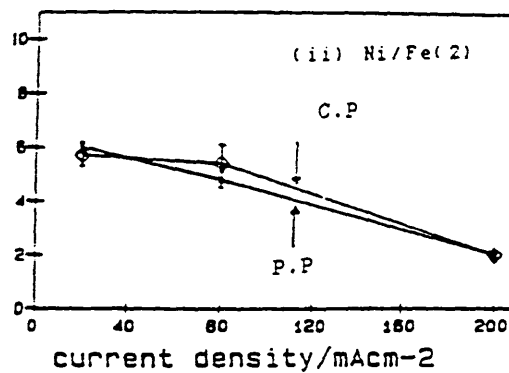
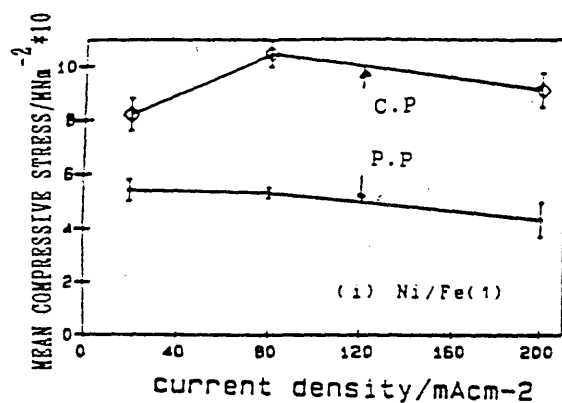


FIGURE 39

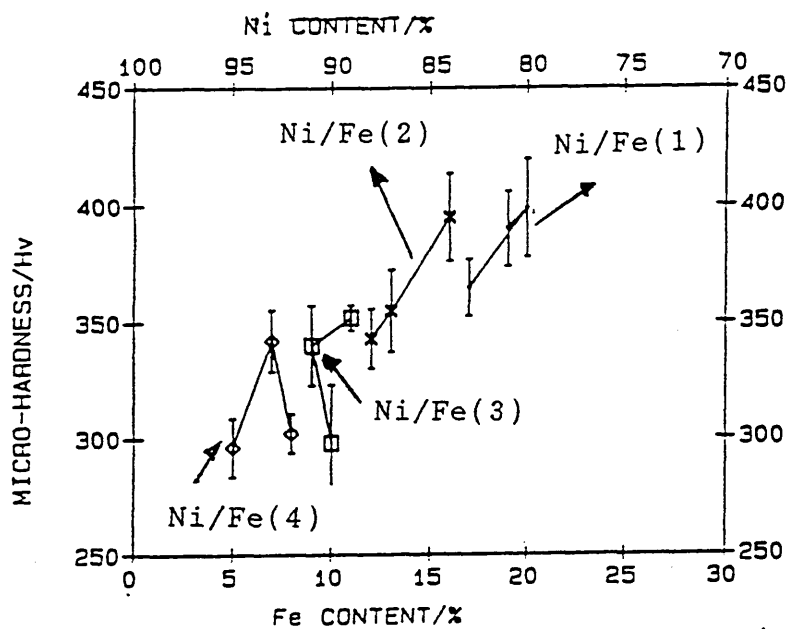
Variation of micro-hardness of the nickel-iron alloy deposits, Ni/Fe(1), Ni/Fe(2), Ni/Fe(3), Ni/Fe(4) with effects of iron, nickel contents, solution pH; (higher pH) and off-time period.

coating thickness=25um

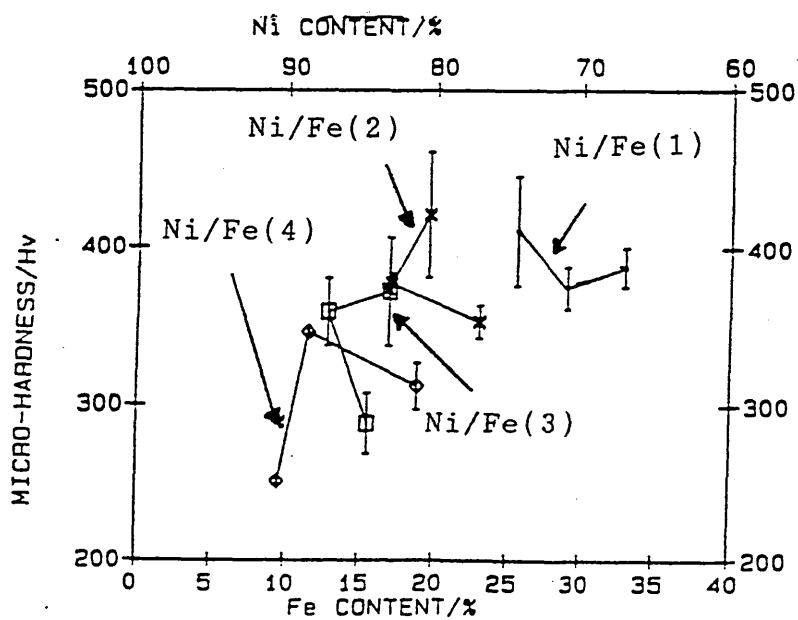
(i)high pH=3.35-3.50

(ii)low pH=2.5-2.8

off-time period=200msec.



(i) High pH



(ii) Low pH

FIGURE 40

Mean internal stress of
nickel/iron and Watts deposits
with effects of plating time,
solution pH and types of
plating, pulse plating(p.p), con-
ventional-plating(c.p).

pH=3.35-3.50 for Ni/Fe and

pH=3.75-4.0 for Watts solutions

coating thickness=3.5um

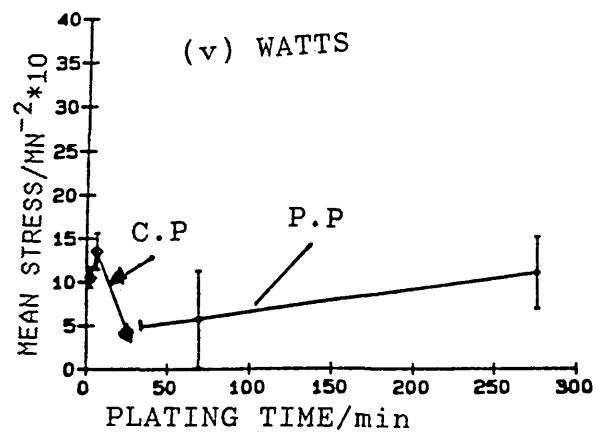
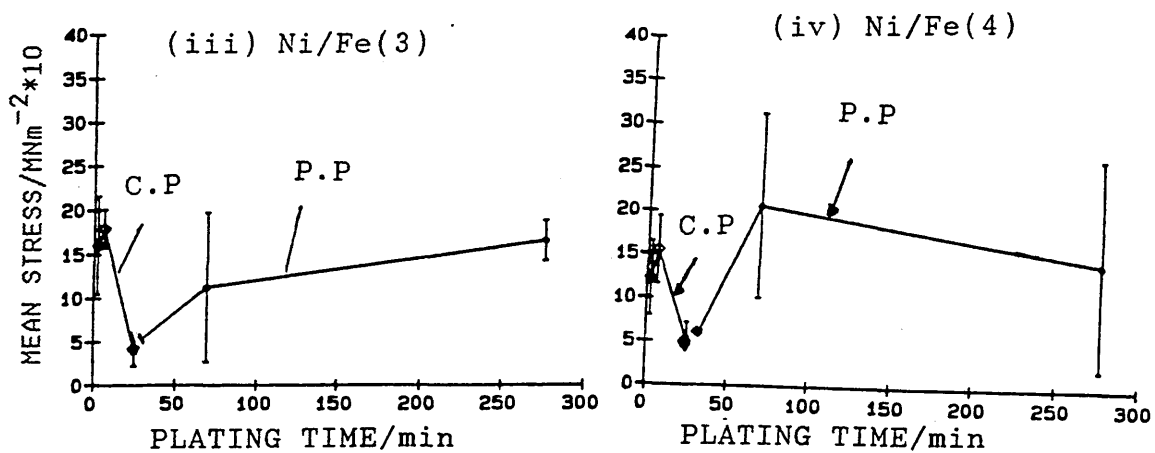
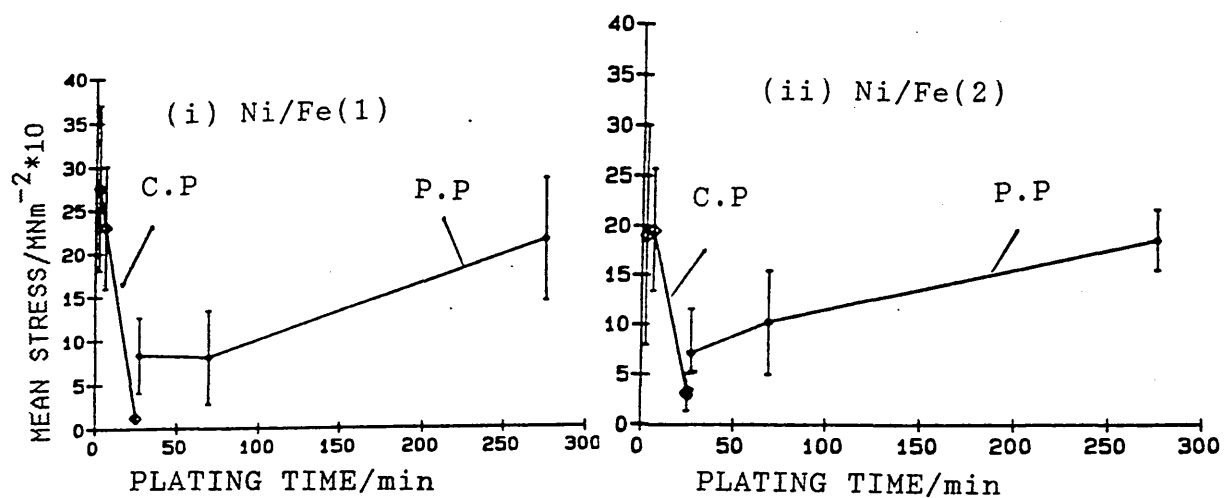


FIGURE 41

Scanning electron micro-graph of
10um nickel deposit with effect
of high current density(250mAcm^{-2})
from Watts bath using pulse
plating. X440

FIGURE 42

Scanning electron micro-graph of
10um nickel deposit with effect
of high current density(250mAcm^{-2})
from Watts bath using pulse
-plating. X1920

FIGURE 43

Flow diagram for pulse-plating and features resulting from pulse-plating method with aid of equipments used. The use of pulse generator, oscilloscope, power Mosfets distinguishes the pulse plating procedure from conventional-plating arrangements.

